

High purity hydrogen generation via partial dehydrogenation of fuels

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High purity hydrogen generation via partial dehydrogenation of fuels

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Abstract

This thesis work have been developed in the general context of the development of more electrified and environmentally friendly means of transport, in order to significantly reduce greenhouse gases emissions. More specifically, the objective of this thesis project was to study the feasibility of the concept of on-board hydrogen generation by catalytic partial dehydrogenation (PDh) of fuel. The hydrogen produced serves to power a fuel cell system that replaces vehicles auxiliary power units. At the same time the fuel, that is only partially dehydrogenated, maintains its properties and can be re-injected into the fuel pool.

This thesis is divided into two main parts. The first part describes the research on the PDh of kerosene to produce hydrogen on-board an aircraft. The choice of the catalyst is crucial: it should allow to produce high purity hydrogen without compromising the original properties of kerosene. Advanced materials, composed by metals impregnated on different supports, have been developed, characterized and evaluated as a catalysts in the reaction of PDh. The influence of catalyst composition on the activity, selectivity and stability as well as the deactivation mechanisms were studied. One of the optimized catalytic materials, composed of a 1% Pt - Sn 1% (w/w) active phase supported on a γ -alumina with controlled porosity, allowed a hydrogen production of 3500 NL·h⁻¹·kg_{cat}⁻¹, with a purity of 97.6% vol. and a lifetime of 79 h, which corresponds to 3.5 kW of electric power supplied by fuel cells.

The second part of the manuscript describes a study on diesel and gasoline and asses the feasibility of hydrogen generation by PDh of fuels different from kerosene. The results obtained with the previously mentioned catalyst are encouraging and show the possibility of applying this concept to other fields of transportation beside the aviation. The most significant results obtained with gasoline and diesel surrogates are respectively a hydrogen productivity value of 3500 et 1800 NL·h⁻¹·kg_{cat}⁻¹ with lifetimes of 29 and 376 h and a purity that exceeds 99% vol. in both cases.

Résumé

Ces travaux des thèse ont été développés dans le contexte général du développement de modes de transport plus électrifiés et plus respectueux de l'environnement, dans le but de réduire considérablement les émissions de gaz à l'effet de serre. Plus particulièrement l'objectif de cette thèse a été d'étudier la faisabilité de la génération d'hydrogène embarquée par déshydrogénation catalytique partielle (PDh) du carburant utilisé dans les moteurs à combustion interne, permettant d'obtenir de l'hydrogène pour alimenter une pile à combustibles embarquée en replacement des unités de puissance auxiliaires. Dans un même temps le combustible qui n'est que partiellement déshydrogéné conserve ses propriétés et peut être réinjecté dans le pool de carburant.

Cette thèse est divisée en deux grandes parties. Une première partie décrit les travaux de recherche sur la déshydrogénation partielle du kérosène pour la production d'hydrogène à bord d'un avion. Le choix du catalyseur est crucial, il doit permettre de produire de l'hydrogène de haute pureté sans compromettre les propriétés d'origine du kérosène. Des matériaux avancés, composés de métaux imprégnés sur des nouveaux supports ont été développés, caractérisés et évalués en tant que catalyseur dans la réaction de PDh. L'influence de la composition du catalyseur sur son activité, sélectivité et durée de vie ainsi que les mécanismes de désactivation ont été étudiés. Un matériau catalytique optimisé composé d'une phase active de 1% Pt - 1 % Sn (m/m) supporté sur une γ -alumine à porosité contrôlée, a permis une production d'hydrogène de 3500 NL·h⁻¹·kg_{cat}⁻¹, avec une pureté de 97,6% vol. et un temps de vie de 79 h, ce qui correspond à une puissance électrique fournie par une pile à combustible de 3,5 kW.

La deuxième partie du manuscrit décrit une étude sur la déshydrogénation de diesel et de l'essence. Les résultats obtenus avec le même matériau sont encourageants et montre une application possible dans des domaines de transports autres que l'aviation. Les résultats les plus significatifs obtenus avec des substituts de gasoil et d'essence sont respectivement des valeurs de productivité d'hydrogène de 3500 et 1800 NL·h⁻¹·kg_{cat}⁻¹ avec des temps de vie de 29 et 376 h et une pureté supérieur à 99 % vol. pour le deux.

Conventions and abbreviations

ABBREVIATIONS	DEFINITION		
AC	Activated Carbon		
ACC	Activated Carbon Cloth		
APU	Auxiliary Power Unit		
ATR	Auto Thermal Reforming		
BET	Braunauer Emmet and Teller		
BJH	Barrett Joyner and Halenda		
СВ	Carbon Black		
CNF	Carbon Nano Fibers		
CGH ₂	Compressed Gaseous Hydrogen		
CNR	Consiglio Nazionale della Ricerca		
CNRS	Centre National de la Reserche Scientifique		
CNT	Carbon Nano Tubes		
CXG	Carbon XeroGel		
DLR	Deutsches zentrum für Luftund Raumfahrt		
DOE	Department Of Energy		
DTA	Differential Thermal Analysis		
EA	Elemental Analysis		
EADS	European Aeronautic Defence and Space company		
EFG	Electric Field Gradient		
EU	European Union		
FC	Fuel Cell		
FID	FID Flame Ionization Detector		
FP7	P7 Framework Program 7		
FWHM	Full Width at Half Maximum		
GC	Gas Chromatograph		
GDP	Gross Domestic Product		
GGE	Gallon of Gasoline Equivalent		
GHG	GreenHouse Gases		
HCs	Hydrocarbons		
HDS	HydroDeSulfuration		
HT	HT HydroTalcite		
IEA	IEA International Energy Agency		
IS	Isomer Shift		
ITF	International Transports Forum		

IUPAC	International Union of Pure and Applied Chemistry		
IWI	Incipient Wetness Impregnation		
LH ₂	Liquefied Hydrogen		
LSK	Low Sulfur Kerosene		
MEA	More Electric Aircraft		
MM	Montmorillonite		
MS	Mass Spectrometer		
MsB	Mössbauer		
NGR	Nuclear Gamma Resonance		
OECD	Organisation for Economic Cooperation and Development		
OMC	Ordered Mesoporous Carbon		
PDh	Partial Dehydrogenation		
PEM	Polymeric Electrolyte Membrane		
POX	Partial Oxidation		
PSA	Pressure Swing Absorption		
QS	Quadrupole Splitting		
SBA	Santa Barbara Amorphous material		
SFK	Sulfur Free Kerosene		
SR	Steam Reforming		
STP	Standard Temperature and Pressure		
TCD	Thermo-Conductivity Detector		
TOF	Turn Over Frequency		
TOS	Time On Steam		
TPD	Thermal Programmed Desorption		
TPR	Thermal Programmed Reduction		
US	United States		
XRD	X-Ray Diffraction		
XRF	X-Ray Fluorescence		

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Résumé Français

A. Introduction générale

Actuellement, la production d'énergie et le secteur des transports sont principalement basés sur l'utilisation de combustibles fossiles mais cette principale source d'énergie voit ses réserves s'épuiser rapidement et d'importantes émissions de gaz à effet de serre (GES) résultent de leur combustion. Afin de réduire la consommation de ces combustibles et de diminuer les émissions polluantes, une solution envisageable serait le développement de véhicules plus électrifiés. Pour générer de l'électricité à bord, une des technologies les plus prometteuses est la pile à combustible embarquée qui présente de nombreux avantages tels qu'un rendement élevé, pas d'émission de GES et aucune nuisance sonore. Actuellement cette technologie est proche d'être commercialisée avec l'intégration des pile à combustible dans les appareils électroniques portables ne nécessitant pas de grandes infrastructures de distribution de l'hydrogène [1,2].

L'adaptation de l'industrie du transport aux piles à combustible et donc à l'hydrogène, en termes de technologie et d'infrastructure, devient donc une possibilité très attrayante car elle contribuera aux défis énergétiques et à la réduction des GES que le monde devra affronter dans l'avenir proche [3–5]. Il est alors possible d'imaginer une interconnexion entre la production d'énergie stationnaire et le secteur des transports, avec la création d'un nouveau système énergétique plus stable et flexible basé sur l'hydrogène [4,6–9].

La production et le stockage de l'hydrogène sont les deux verrous technologiques à lever pour permettre le développement d'un tel système énergétique. Actuellement, les méthodes de production de l'hydrogène sont chères, peu efficaces et impactent négativement l'environnement. Ainsi, 95% de la production est réalisée à partir de combustibles fossiles, par reformage du gaz naturel [10]. Un autre facteur important à considérer est que la plupart de l'hydrogène est actuellement utilisé pour des applications industrielles et son application au secteur des transports signifierait une forte augmentation de la demande. Cependant cela peut favoriser une exploitation à plus grande échelle des ressources renouvelables: l'énergie produite par ces sources (photovoltaïque, éolien, hydroélectrique) est intermittente donc plus complexe à exploiter, mais il y a la possibilité de l'utiliser pour la production d'hydrogène [11].

Le stockage de l'hydrogène représente aussi un enjeu de taille. En effet, même si l'hydrogène a la densité énergétique massique la plus élevée parmi les différents combustibles (143,0 MJ/kg, trois fois plus que l'essence), l'hydrogène gazeux a également la plus faible densité d'énergie volumique (0,0108 MJ/L, 3000 fois plus petit que l'essence). D'autre part, il peut exploser violemment lorsqu'il est mis en contact avec l'air [12]. Trouver un moyen sûr et économique pour le stocker et le rendre disponible pour de telles applications représente donc un défi. En particulier pour les applications embarquées, il y a une contrainte stricte liée à l'espace nécessaire en vue d'une certaine autonomie requise [4,13,14]. Différentes possibilités de stockage d'hydrogène sont en cours de développement: le confinement mécanique (hydrogène comprimé, cryo-comprimé ou hydrogène liquide), la physisorption dans des matériaux poreux et l'utilisation d'hydrures chimiques. Le stockage mécanique reste actuellement l'approche le plus réalisable, mais un grand effort est encore nécessaire en termes de poids et qualité des matériaux des réservoirs de stockage [6,15].

Une alternative au stockage, particulièrement avantageuse pour les transports, pourrait être la génération de l'hydrogène directement à bord. Parmi les différents processus de production d'hydrogène, un des plus prometteurs est la déshydrogénation catalytique d'hydrocarbures liquides. Par exemple, les cycloalkanes ont une capacité d'hydrogène relativement élevée à la fois en poids et en volume (généralement plus de 5% en poids et 50 g L⁻¹). Comme les cycloalcanes sont liquides à conditions ambiantes, les infrastructures déjà existantes pour le transport, le stockage et la distribution des autres carburants peuvent être utilisées. Ceci et la présence déjà importante de systèmes

d'hydrogénation/déshydrogénation devraient permettre de réduire les coûts d'investissement pour la mise en place d'un tel système de distribution d'hydrogène. Un autre avantage est que l'hydrogène fourni par ce procédé est de très haute pureté et sans trace de CO ou CO_2 , ce qui permet l'alimentation directe de piles à combustible [16–19].

Ce travail de thèse a été effectué dans un contexte général de développement de moyens de transport plus électrifiés et plus écologiques, afin de réduire considérablement les émissions de GES. Plus précisément, l'objectif de ce projet était d'étudier la faisabilité du concept de génération d'hydrogène à bord par déshydrogénation catalytique partielle (PDh) de carburants. L'hydrogène produit servirait à alimenter une pile à combustible intégrée en remplacement des actuelles unités de puissance auxiliaires des véhicules (APU: Auxilary Power Unit). Dans un même temps, le combustible qui n'est que partiellement déshydrogéné conserverait ses propriétés de carburant et pourrait être réinjecté dans le réservoir et brulé dans les moteurs.

Cette thèse est divisée en deux parties principales. La première partie, qui a commencé dans le cadre du projet européen "GreenAir" (FP7 transport, convention de financement n° 233862), décrit la recherche effectuée sur la déshydrogénation catalytique partielle de kérosène pour produire de l'hydrogène à bord d'un avion. L'hydrogène produit sera utilisé pour alimenter un système de pile à combustible à membrane échangeuse de protons (PEM) qui se substitue au système APU de l'avion. Le choix du catalyseur est fondamental car il doit permettre de produire de l'hydrogène de haute pureté, sans compromettre les propriétés d'origine du kérosène. Des matériaux avancés, à base de métaux (notamment de Pt et Sn) imprégnés sur différents supports ont été développés, caractérisés et évalués en tant que matériaux catalytiques, dans la réaction de déshydrogénation partielle. L'influence de la composition du catalyseur sur la convertion en hydrogène et la sélectivité ainsi que les mécanismes de désactivation du matériau ont été étudiés. La seconde partie du manuscrit décrit une étude concernant l'essence et le gazole et démontre la faisabilité de la production d'hydrogène par déshydrogénation

catalytique partielle de combustibles différents du kérosène. Les résultats encourageants montrent la possibilité d'appliquer ce concept aux autres moyens de transport.

B. Génération d'hydrogène à bord par déshydrogénation partielle de carburant

I - Introduction

Dans le but d'approvisionner en hydrogène des piles à combustible embarquées, la réaction de déshydrogénation catalytique partielle peut être effectuée sur un mélange complexe d'hydrocarbures comme le kérosène, le gasoil, le naphta ou l'essence. Une fraction du combustible contenu dans les réservoirs du véhicule serait alors partiellement déshydrogénée afin de produire l'hydrogène nécessaire. En effet, avec une déshydrogénation contrôlée, il n'y aura pas de changement considérable des propriétés du carburant déshydrogéné qui sera toujours apte à l'utilisation comme carburant dans les moteurs à combustion. Un brevet décrivant ce processus a été déposé par Airbus [20]. L'utilisation des piles à combustible est prévue en remplacement des turbines et des alternateurs pour la production d'électricité, permettant ainsi d'augmenter l'efficacité globale du système et par conséquence d'optimiser l'utilisation du carburant et de réduire les émissions de GES. Un schéma simplifié du processus de déshydrogénation catalytique partielle (PDh) de carburants est rapporté en Fig. 1.



Figure 1 - Schéma du processus de déshydrogénation partielle de carburants

Outre la possibilité de réutiliser le combustible après la réaction, cette nouvelle technologie de traitement du combustible présente de nombreux avantages par rapport aux technologies de reformage. Le système de PDh est plus compact par rapport aux unités de reformage classique et l'hydrogène produit par PDh est quasiment pur et ne contient pas de CO. Ceci évite la nécessité d'installer une unité de purification volumineuse qui est nécessaire pour les procédés de reformage. Les produits de la déshydrogénation catalytique partielle sont uniquement de l'hydrogène et le combustible déshydrogéné; cela représente un avantage certain par rapport aux procédés de reformage qui produisent également de grandes quantités de CO et CO₂. En conséquence, le processus de PDh ne nécessite pas de réacteur de WGS (water gas-shift) supplémentaire, requis dans le cas du reformage de carburants, ce qui rend ce processus encore plus compact et pratique.

La déshydrogénation catalytique partielle du kérosène est une technologie très récente, un intérêt croissant y est porté depuis les études réalisées pendant le projet européen "GreenAir" et plusieurs articles peuvent être trouvé dans la littérature [21–26]. En principe, il est possible alimenter un système embarqué de piles à combustible par déshydrogénation partielle de kérosène Jet A-1, sans la nécessité d'avoir des réservoirs d'hydrogène. Dans ce procédé, seule une quantité suffisante d'hydrogène, nécessaire à l'alimentation de la pile à combustible et donc à la génération de l'électricité est prélevée. Comme déjà mentionné, les avantages de cette méthode sont la grande pureté de l'H₂, l'absence de CO/CO_2 et la possibilité de réutiliser le kérosène déshydrogéné.



Figure 2 - Schème de un avion avec une APU à pile a combustible alimentée par un réacteur de PDh

La déshydrogénation partielle catalytique de combustibles autres que le kérosène n'a actuellement jamais été réalisée. Il n'existe pas de publication concernant cette réaction dans la littérature. L'application à d'autres types de véhicules qu'un avion implique une étude de faisabilité pour adapter le processus à d'autres types de carburants tels que l'essence et le gazole.



Figure 3 - Application de la technologie de déshydrogénation partielle de carburants aux transports routiers

II. Déshydrogénation partielle de kérosène

II.1. Procédé catalytique et optimisation des matériaux

Les conditions optimales de fonctionnement pour la réaction de désydrogénation partielle du Low Sulfur Kerosene (LSK: kerosene désoufré contenant 3 ppm massique de soufre), avec des catalyseurs de Pt-Sn supportés, sont les suivantes: $T = 450 \circ C$, P = 1 MPa, $\tau = 2s$, recyclage d'hydrogène = 7% vol. mélangé aux vapeurs de LSK (avant de l'évaporateur). Des températures plus élevées favorisent les réactions secondaires telle que le craquage d'hydrocarbures, ce qui est indésirable car le dépôt de coke qui est généré cause une rapide désactivation du catalyseur. A l'inverse, des températures plus basses ne permettent pas une productivité d'hydrogène suffisante. En raison des spécifications techniques, la pression a été fixée à une valeur de 1 MPa. Le temps de contact (τ) et le recyclage de l'hydrogène ont été réglés afin d'obtenir le meilleur compromis entre la productivité de l'hydrogène, sa pureté et la stabilité du catalyseur.

L'évaluation d'une série de différents supports a mis en évidence que la porosité du matériau est un aspect essentiel pour l'activité et la stabilité. Les pores très petits, dont la taille est proche de celle des micropores (< 2 nm), sont plus facilement bouchés par les phénomènes de dépôt de coke. Les matériaux mésoporeux, avec un volume de pores élevé, semblent être les candidats idéaux pour la réaction de déshydrogénation partielle de carburants. Parmi eux, les résultats montrent que la γ -Al₂O₃ représente un excellent compromis entre le coût, et la facilité de synthèse et l'activité en PDh.

L'acidité des matériaux est un autre facteur important qui affecte les propriétés catalytiques. Il a déjà été observé que la prévalence des sites acides forts est nuisible à la réaction de PDh. Ceux-ci peuvent catalyser les réactions de craquage qui conduisent à la formation de précurseurs de coke [27,28]. La présence de sites acides moyens peut elle, augmenter la productivité

d'hydrogène en catalysant les réactions d'isomérisation et de cyclisation [29]. Une valeur d'acidité optimale semble être de l'ordre de 100-200 μ molNH₃·g⁻¹.

Deux catalyseurs de Pt-Sn (1% - 1% m/m) supportés sur γ -Al₂O₃ (JM1) et BaO/Al₂O₃ (JM2) ont été synthétisé par Johnson&Matthey et ont été utilisé comme référence pour les autres matériaux catalytiques dans la réaction de PDh de LSK.

Optimisation du catalyseur par modification de la phase métallique

Le catalyseur bimétallique de Pt-Sn/ γ -Al₂O₃ a été optimisé par l'introduction d'indium en tant que troisième métal: une série des catalyseurs (Cat-In[x]) à différente teneur en indium (0-1 % m/m) a été synthétisé et testé. Les catalyseurs trimétalliques Pt-Sn-In/ γ -Al₂O₃ montrent une réactivité différente qui conduit à une amélioration de la stabilité. En particulier, une remarquable amélioration de la productivité d'hydrogène et de la durée de vie du catalyseur ont été mesurées pour un catalyseur avec une teneur en métal Pt:Sn:In de 1:1:0,5 en masse. Avec ce nouveau type de matériau, la proportion des métaux à l'état réduit est augmentée et l'activité vis-à-vis de la réaction de déshydrogénation est ainsi améliorée. Le nombre de sites acides forts est réduit, limitant ainsi les réactions secondaires indésirables. Par conséquent, la formation de coke est limitée, entrainant une nette amélioration de la stabilité. Plus spécifiquement, la présence d'indium semble diminuer la quantité de coke formé à proximité de particules de Pt.

Optimisation du catalyseur par modification du support mesoporeux

Un nouveau processus à faible coût et facilitant la mise à l'échelle industrielle a été optimisé pour la synthèse de γ -Al₂O₃ en utilisant le saccharose comme matrice. Ce procédé sol-gel a lieu en solution aqueuse de saccharose qui agit comme agent structurant non tensioactif, conduisant à la formation de la porosité du matériau. Le catalyseur obtenu a partir de ce nouveau support alumine (ALUSUC2[PtSn]) montre une surface spécifique et une dispersion métallique supérieurs à celles du matériau de référence.

II.2. Résultats obtenus en termes de production d'hydrogène

En utilisant le catalyseur Cat-In[0.5] une production d'hydrogène moyenne de 2900 NL·h⁻¹·kg_{cat}⁻¹ a été obtenue lors d'un test de 6 h. La pureté de l'hydrogène après 6 h de réaction était de 97.8% vol. avec CH₄ comme impureté principale ainsi que des traces d'hydrocarbures C₂-C₄. La durée de vie extrapolée à partir de l'interpolation linéaire de la courbe de productivité entre 120-360 min TOS est de 107 h. En utilisant le catalyseur ALUSUC2[PtSn] une production d'hydrogène moyenne de 3500 NL·h⁻¹·kg_{cat}⁻¹ a été obtenue avec une pureté d'hydrogène de 97.6% vol. La durée de vie extrapolée est de 79 h. Il en résulte une amélioration remarquable par rapport aux matériaux de référence utilisés dans le cadre du projet "GreenAir": le matériau de deuxième génération JM2 avait une productivité moyenne de 2500 NL·h⁻¹·kg_{cat}⁻¹ avec une durée de vie de 35 h et une pureté de l'hydrogène de 97.2% vol.



Figure 4 - Productivité d'hydrogène pour les matériaux optimisés et de référence

Dans le cadre du projet "GreenAir", une étude sur la PDh de kérosène était requise afin d'atteindre différents objectifs techniques, certains liés à la partie de la catalyse et d'autres à l'ingénierie du système. Ces objectifs sont présentés dans le Tableau 1 ainsi que les résultats obtenus avec ALUSUC2[PtSn] et Cat-In[0.5].

PARAMETRE	OBJECTIF	ALUSUC2[PtSn]	Cat-In[0.5]
Production $d'H_2$ (NL·h ⁻¹ ·kg _{cat} ⁻¹)	1000	3500	2900
Puissance electrique (kWe)	1	3.5	2.9
Temps de vie (h)	100	79	107
Pureté de l'H ₂ (% vol.)	> 95	97.6	97.8
Tolérance au soufre (ppm)	300	3	3
Temps de démarrage (min)	< 15	≈ 30	≈ 30

Tableau 1 - Evaluation des résultats de PDh de kérosène obtenus avec ALUSUC2[PtSn] et Cat-In[0.5]

La productivité d'hydrogène, sa pureté et la durée de vie du catalyseur sont suffisantes pour atteindre l'objectif visé. Le temps de démarrage du banc de test de laboratoire de 30 min est lié aux temps de stabilisation de la température de chauffage et de la mise sous pression du système. Dans un réacteur pilote à plus grande échelle, des dispositifs de contrôle du chauffage et de la pression plus efficaces pourront réduire le temps de démarrage à moins de 15 min. Les résultats obtenus ont montré que la déshydrogénation partielle catalytique de kérosène est une technologie embarquée prometteuse pour la production directe d'hydrogène à haute pureté.

Cependant l'activité des catalyseurs est très sensible à la présence de soufre et les essais ont été effectués avec un kérosène à faible teneur en soufre (LSK 3 ppm de S), plus cher et commercialement moins et surtout inégalement disponible dans tous les pays. Dans la perspective d'un développement mondial de cette technologie, l'utilisation du Jet A-1 standart (2000 ppm S) est primordiale. Un nouveau catalyseur thiorésistant doit être développé pour des combustibles riches en soufre oubien une étape de désulfuration doit être ajoutée avant la réaction de PDh. La fractionnation thermique du Jet A-1 standart par rectification peut aussi être une solution alternative. Ce procédé de distillations successives permet de séparer les composants et sélectionner ceux adaptés à la PDh. La concentration des hydrocarbures cycliques est augmentée, et une grande partie du soufre est éliminé avant la réaction de PDh ayant la conséquence d'augmenter la production d'hydrogène.

La chaleur de combustion du kérosène déshydrogéné n'a pas été mesurée, mais le combustible nécessaire à la réaction de PDh est une petite fraction du volume total de carburant contenu dans les réservoirs (ex. capacité de carburant de un Airbus A320 \approx 25000 L). Il est possible de démontrer que le kérosène déshydrogéné, après avoir été mélangé à une partie du combustible d'origine, permettra d'avoir des propriétés de combustion qui sont encore dans les spécifications pour le Jet A-1.

II.3. Perspectives futures

Les résultats obtenus sont encourageants pour la poursuite de projets de recherche sur ce sujet. La majorité des objectifs définis au début du projet ont été atteints. D'autres améliorations du procédé et des matériaux catalytiques doivent être effectuées. En particulier la modification du catalyseur ALUSUC2[PtSn] avec ajout d'indium est l'une des premières possibilités à considérer.

La partie d'ingénierie du système embarqué pour la construction d'un réacteur pilote incluant le système des piles à combustible est également très important pour déterminer la faisabilité à bord des avions: l'espacement et le dimensionnement, le poids, l'échange et la récupération de chaleur sont des facteurs clés qui déterminent le coût et l'efficacité du système.

III. Déshydrogénation catalytique partielle de l'essence et du gazole

III.1. Déshydrogénation partielle d'un modèle d'essence (surrogate d'essence)

Les études sur la réaction de déshydrogénation partielle de deux modèles d'essence ont mis en évidence que le matériau ALUSUC2[PtSn] est très sensible à la présence d'éthanol dans le mélange. Les tests catalytiques effectués avec l'essence A, contenant 3,5% vol. d'EtOH, montrent une désactivation très rapide. Le mécanisme envisagé consiste en la déshydratation de l'éthanol en éthylène, qui par polymérisation peut amener à la formation des précurseurs de coke et provoque donc la désactivation du catalyseur. Cette hypothèse est étayée par analyses d'ATG/ATD. Les analyses effectuées sur les catalyseurs après réaction avec l'essence A (avec EtOH), montrent une quantité de coke déposée qui est trois fois plus élevée par rapport à la réaction avec l'essence B (sans EtOH). En particulier, un large pic exothermique à basse température (225 °C) est observé pour le modèle A, qui pourrait être attribué à la combustion d'un type de coke formé par polymérisation d'éthylène. Une autre confirmation vient de l'analyse de la pureté de l'hydrogène produit, qui montre une quantité considérable d'impuretés C₂ lors de la réaction avec le modèle A.

Les conditions de fonctionnement optimales identifiées pour la PDh du modèle d'essence B avec le catalyseur ALUSUC2[PtSn] sont les suivantes: 400 °C, 0.1 MPa, $\tau = 2s$ et 7% vol. recyclage H₂. La température de 400 °C a été choisie parce qu'elle permet la conversion totale des hydrocarbures cycliques (qui sont la principale source de H₂) et permet également d'obtenir la plus haute sélectivité pour la réaction de déshydrogénation. La pression choisie est de 0.1 MPa, afin d'avoir une légère surpression qui permet de passer facilement de l'hydrogène produit, à la pile à combustible. L'introduction d'une phase de recyclage d'une petite quantité d'hydrogène (7% vol.) a pour effet d'augmenter remarquablement la durée de vie du catalyseur en réduisant la formation de coke.

Avec le modèle d'essence B, une production moyenne d'hydrogène de 1800 NL·h⁻¹·kg_{cat}⁻¹ est obtenue avec une pureté supérieure à 99% vol. et une durée de vie du catalyseur de 376 h.

III.2. Déshydrogénation partielle d'un modèle de gazole (surrogate de gazole)

Les études de la réaction de déshydrogénation partielle de modèles de gazole ont souligné que la stabilité du matériau ALUSUC2[PtSn] est fortement affectée par la présence d'un type spécifique de naphtène dans le mélange. Les tests catalytiques effectués sur le modèle A, contenant 7% vol. de 1-méthyl-naphtalène, montrent une désactivation très rapide. Le mécanisme envisagé consiste en la formation d'un radical bi-cyclique, qui forme par polycondensation un dépôt de coke responsable de la désactivation par occlusion des pores. Cette hypothèse est étayée par les résultats d'ATG/ATD. La quantité de coke formé après réaction avec le modèle A (contenant 1-méthyl-naphtalène) est beaucoup plus élevé qu'après la réaction avec le modèle B (sans 1-méthyl-naphtalène). Un pic important de combustion du coke à 450 °C est observé et cela peut être attribué à un type de coke formé par polycondensation du 1-méthyl-naphtalène. Ce pic n'est pas présent dans le cas du modèle de diesel B où le 1-méthyl-naphtalène a été remplacé par la tétraline en tant que représentant de la classe de naphtene.

Les conditions de fonctionnement optimales identifiées pour la PDh du modèle de l'essence B avec le catalyseur ALUSUC2[PtSn] sont les suivantes: 400 °C, 0.1 MPa, $\tau = 2s$ et 7% vol. recyclage H₂. De façon similaire a ce qui a été observé pour l'essence, la température de 400 ° C a été choisie car elle permet une conversion presque complète des hydrocarbures cycliques (la source principale de H₂) et une haute sélectivité pour la réaction de

déshydrogénation. Une température plus élevée permet une meilleure conversion, mais la pureté de l'hydrogène est diminuée car des réactions secondaires (craquage pour exemple) commencent à être favorisées. La valeur de pression choisie est de 0.1 MPa. Un recyclage de 7% vol. d'hydrogène augmente la durée de vie du catalyseur, mais pas aussi nettement que pour l'essence.

Avec le modèle B de diesel, une production moyenne d'hydrogène de $3500 \text{ NL} \cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$ avec une pureté supérieure à 99% vol. et une durée de vie de 29 h est obtenue.

III.3. Comparaison entre les réactivités des différents modèles de carburants

Un test catalytique a été effectué avec un modèle du kérosène (utilisé dans les études préliminaires du projet "GreenAir") et les résultats ont été utilisés comme référence pour l'évaluation des résultats obtenu avec les modèles de gazole et d'essence. Il a été montré que ce kérosène a un comportement très semblable à celui du kérosène réel (LSK) dans les conditions de la réaction de PDh. La productivité d'hydrogène, sa pureté et la stabilité du catalyseur pour la réaction avec le LSK sont légèrement inferieures à celles du modèle contenant cinq composants. Cette différence est attribuée à plusieurs facteurs: la plus grande complexité de la composition chimique, la présence de soufre (ppm \approx 3) et la présence d'additifs dans le LSK. En effet, le temps de vie extrapolée est réduit de 156 h à 79 h, la pureté de 99,3% vol. à 97,6% et la productivité de 3700 NL·h⁻¹·kg_{cat}⁻¹ à 3500 NL·h⁻¹·kg_{cat}⁻¹. Cependant, en dépit de ces différences, il est possible d'affirmer que ce modèle de kérosène est bien représentatif du carburant LSK.

Les resultats en termes de productivité et de pureté d'hydrogène ainsi qu'en durée de vie du catalyseur, obtenu avec le modèle de kérosène et les modèles B de d'essence et de gazole sont montré en Fig. 5:



Figure 5 - Productivité d'hydrogene pour les differents modèles de carburants avec ALUSUC2[PtSn]

La stabilité du catalyseur et la productivité d'hydrogène sont inversement proportionnelles entre elles et sont liées à la longueur de chaîne carbonée des hydrocarbures déshydrogénés. Le gazole B, qui a une longueur de chaîne carbonée moyenne plus élevés que les autres, est le mélange qui a montré la plus haute productivité d'hydrogène initiale ($\approx 3800 \text{ NL} \cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$) et le temps de vie le plus court (29 h). Le kérosène, qui est le deuxième en termes de longueur de chaîne carbonée, a montré une productivité initiale d'hydrogène intermédiaire ($\approx 3500 \text{ NL} \cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$), mais un temps de vie largement supérieur (156 h) par rapport au gazole B. Enfin, en terme de longueur de chaîne, le modèle d'essence B montre la valeur la plus faible de productivité d'hydrogène (1800 NL $\cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$), mais le temps de vie le plus important (376 h).

Les hydrocarbures à longue chaîne semblent être plus facilement soumis à des réactions non souhaitées, comme le craquage, ce qui cause la désactivation du catalyseur par déposition de coke.

La réactivité des différents modèles de carburants depend de la composition des hydrocarbures contenus dans chaque mélange. Comme est

montré en Fig. 6 (qui impliquerait un réacteur contenant 1 kg de catalyseur) la production totale est similaire pour les modèles de kérosène et gazole avec une valeur proche de 5,4 NL·min⁻¹ et inférieure pour le modèle d'essence avec une valeur proche de 3 NL·min⁻¹. Le point commun est que la majorité de l'hydrogène produit provient de la déshydrogénation des molécules cycliques qui sont plus réactives. Les hydrocarbures cycliques et bi-cycliques sont déshydrogénés, conduisant à des composés aromatiques ou polyaromatiques montrant des valeurs de conversion comprises entre 80-100% et une sélectivité du 100%. Les molécules linéaires, dans le cas de kérosène et gazole, apportent une très petite contribution et conduisent à très peu de conversion. L'exception est faite pour l'essence où les hydrocarbures linéaires courts (C₇-C₈) contribuent de manière plus significative à la production d'hydrogène grâce a des étapes de dehydrocyclisation-aromatisation.



Figure 6 - Production d'hydrogène par classe d'hydrocarbure pour les modèles de carburant

III.4. Applications futures et perspectives

Les études préliminaires sur la PDh de l'essence et du gazole pour la production d'hydrogène à haute pureté ont amené à des résultats encourageants. L'efficacité du procédé est reliée directement à la présence de certains composés dans le combustible: dans le cas de l'essence la présence

d'éthanol est un frein à l'utilisation de ces catalyseurs. Dans le cas du gazole la stabilité dépend du type de naphtènes présents dans le mélange. Les résultats obtenus avec le modèle d'essence B (sans EtOH) sont particulièrement remarquables avec notamment une productivité d'hydrogène satisfaisante (1800 NL·h⁻¹·kg_{cat}⁻¹, pureté> 99% vol.) et un temps de vie du catalyseur excellent (376 h).

Les prochaines étapes de cette étude seront l'évaluation de la réaction de PDh sur l'essence et le gazole standart mais aussi sur des biocombustibles commerciaux afin de vérifier les résultats préliminaires obtenus avec les modèles. Comme observé pour les études sur le kérosène, la composition chimique est plus complexe pour les carburants que pour les modèles et d'autre part la présence d'additifs dans les carburants peut aussi modifier les résultats de la réaction de PDh. En parallèle l'optimisation des materiaux catalytiques doit être poursuivi afin d'obtenir une activité et stabilité encore meilleures.

IV. Conclusions

Dans ce travail de thèse, deux matériaux montrent des bonnes performances dans la réaction de déshydrogénation partielle de kérosène: un catalyseur trimétallique de 1% Pt-1% Sn-0,5% In/γ -Al₂O₃ (Cat-In [0,5]) supporté sur une alumine commerciale dans lequel l'indium permet une amelioration de la stabilité et reactivité de la phase active; un catalyseur bimétallique de 1% de Pt-1% Sn/ γ -Al₂O₃ (ALUSUC2[PtSn]) supporté sur une nouvelle matrice d'alumine obtenue avec du saccharose comme agent structurant qui permet la formation d'une porosité optimisé pour la dispersion de la phase active et la resistance au cokage.

Ces deux materiaux montre une productivité et pureté d'hydrogène, ainsi qu'une durée de vie de catalyseur, suffisantes pour atteindre l'objectif visé.

La déshydrogénation partielle de combustibles autres que le kerosene, effectuée avec le catalyseur ALUSUC2[PtSn] a montré une importante productivité d'hydrogène de haute pureté. En particulier pour l'essence, le dépôt de carbone sur le catalyseur est faible et la durée de vie du catalyseur est superieure à 350 h.

La réactivité des différents combustibles est lié à composition en hydrocarbures. Les hydrocabures cycliques sont la principale source d'hydrogène mais la reactivité est aussi affecté par la distribution de la longueur de chaîne. Des hydrocarbures plus lourds contribuent plus à la production d'hydrogene mais sont aussi plus facilement sujets a des réactions secondaires qui provoquent la formation de coke et donc à la désactivation du catalyseur.

Les résultats de cette étude permettent d'affirmer que la déshydrogénation partielle des combustibles est une méthode efficace de génération d'hydrogène à bord, permettant l'alimentation de piles à combustible embarquées.
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1. Introduction

1.1 General introduction

Currently the energy production and the transportation sector mainly rely on fossil fuels, but those cannot continue to be the primary energy source because the reserves are rapidly depleting and significant emissions of greenhouse gases result from their combustion. One of the principal users of fossil fuels are motorized vehicles, which burn fuels in an internal combustion engine. In order to reduce the fossil fuels consumption and the polluting emissions of the transport sector a possible solution would be to go in the direction of more electrified vehicles. At the moment one of the most promising technologies for the generation of electricity on-board are proton exchange membrane (PEM) fuel-cells, which present many advantages as the high efficiency, the absence of greenhouse gases (GHG) emissions and the quietness. Fuel-cells technology is already close to entering the market with some portable electronic devices (pc batteries, walkie-talkies, gps) that don't need big distribution infrastructures [1,2].

As results, the adaptation of the transport sector to hydrogen, in terms of technologies and infrastructures, is a very appealing possibility because it would give a fundamental contribution to the challenges of energy supply and greenhouse emissions reduction that the world will have to face in the near future [3–5]. It is possible to imagine in the future the interconnection of stationary energy production to the transport system, creating a new more stable and flexible energetic system based on hydrogen [4,6–9].

The two main issues for the actuation of such an energy system based on hydrogen are its production and storage. At the moment, the majority of the H_2 comes from fossil fuels (more than 90 %) and the principal method of production is the steam reforming of natural gas from which around 50 % of it is obtained [10]. Another important factor to consider is that most of the hydrogen is currently used for industrial applications and the application to the transport sector would mean a great increase of the demand, but this may favour a wider scale exploitation of renewable resources: the energy produced by these sources (photovoltaic, aeolian, hydroelectric) is intermittent so more complex to exploit, but there is the possibility to store it producing hydrogen [11].

The second obstacle to overtake is the storage, in fact even though hydrogen has the highest energy density of common fuels by weight (143.0 MJ/kg, three times larger than gasoline), unfortunately, with 0.0108 MJ/L, gaseous H₂ also has the lowest energy density by volume (over 3000 times smaller than gasoline) and it can explode violently when brought into contact with air [12]. This means a big challenge to find a safe and economic way to store it and make it available for applications of interest. In particular for onboard application in transports, there are strict constraint related to space and autonomy range [4,13,14]. There are different possible solutions for hydrogen storage that are under investigation: mechanical confinement (compressed, cryocompressed, liquid hydrogen), physisorption in porous materials and using chemical hydrides. The closest to the specifications assessed for the feasibility of the system is currently the mechanical storage, but a great effort is still needed in terms of research of better materials for this purpose [6,15].

An alternative to the hydrogen storage, particularly advantageous for transports, could be the direct on-board generation of hydrogen. Among the different process for the hydrogen delivery to fuel-cells, a promising one is the catalytic dehydrogenation of liquid hydrocarbons (HCs). The most studied HCs are cycloalkanes, which have a relatively high hydrogen capacity on both the weight and volume basis (generally over 5 wt % and 50 g L⁻¹). As cycloalkanes are in liquid phase at ambient conditions their transportation can exploit the existing infrastructures (pipelines, lorries, trains, boats) and the wide presence of hydrogenation/dehydrogenation facilities would further decrease the investment costs for the actuation of such a hydrogen delivery system. Another advantage is that the hydrogen delivered with this method has high purity and is CO and CO₂ free allowing the direct alimentation of fuel-cells [16–19].

This thesis work has been developed in the general context of the development of more electrified and environmentally friendly means of transport, in order to significantly reduce greenhouse gases emissions. More specifically, the objective of this thesis project was to study the feasibility of the concept of on-board hydrogen generation by catalytic partial dehydrogenation (PDh) of fuel. The hydrogen produced serves to power a fuel cell system that replaces vehicles auxiliary power units (APU). At the same time the fuel that is only partially dehydrogenated maintains its properties and can be re-injected into the fuel pool.

This thesis is divided into two main parts. The first part, started in the frame of the European project "GreenAir" (FP7 transport, grant agreement n° 233862), describes the research on the PDh of kerosene to produce hydrogen on-board an aircraft. The hydrogen produced will be used to feed a PEM fuelcell system that substitute the classic turbine APU of the plane. The choice of the catalyst is crucial because it should allow to produce high purity hydrogen without compromising the original properties of kerosene. Advanced materials, composed by metals (mainly Pt and Sn) impregnated on different supports have been developed, characterized and evaluated as a catalyst in the reaction of PDh. The influence of catalyst composition on the activity, selectivity and stability as well as the deactivation mechanisms were studied. The second part of the manuscript describes a study on diesel and gasoline and assesses the feasibility of hydrogen generation by PDh of fuels different from kerosene. The encouraging results obtained in the first part of the work show the possibility of applying this concept to other fields of transportation beside the aviation.

1.2 Environmental and economical context

Nowadays the energy production and the transports sectors are responsible for the majority of the deleterious emissions accompanied by a number of environmental inconveniences. As illustrated in Fig. 1, the percentage of electricity generated from renewable resources is increasing in the last decades, but is still a small fraction of the electricity produced worldwide. The majority of the electricity is still produced by combustion of fossil fuels and, if the growth rate continues without changes in our energy system, the energy demand is destined to increase in the future [3,5,20].



Figure 1 - World electricity generation evolution by fuel (TWh) [3]

The combustion of fossil fuel, both for electricity generation and transportation, is the principal contribution to the emission of greenhouse gases and, in terms of CO_2 emissions only, those are responsible for the 99,6 % of it (Fig. 2) [3,5,20].



Figure 2 - World CO₂ emissions by fuel (MTon)[3]

As reported by Barnstein et. al. [5] in 2004, the emission of all the GHG produced by human activity come from many different sectors, but the main contribution is caused by the energy supply sector (25.9 %) because of the wide use of fossil fuels for energy production. Energy supply and transport sectors together are responsible for the 39 % of those emissions (Fig. 3).



Figure 3 - Contribution to greenhouse gas emissions by sector in 2004 [5]

A more recent report written by the "International Transport Forum" in 2006 [20] asses that, in terms of CO_2 emissions only, the transport and energy

supply sector would be responsible together for the 69.5 %. The CO_2 share coming from transportation (24 %) is principally due to road transportation (16.7 %), then aviation (3.4 %) and maritime (3.4 %). A diagram summarising the data is showed in Fig. 4.



Figure 4 - World CO₂ Emissions from Fossil Fuel Combustion in 2006 [20]

Transport is the second largest CO_2 -emitting sector after energy generation. In OECD (Organisation for Economic Cooperation and Development) countries, the average share of transport CO_2 emissions was around 26 % in 2006 even though some countries displayed very different shares. Much of the growth in emissions has been in step with GDP (Gross Domestic Product) growth and the resultant increase in numbers of vehicles and international travels. Among the different transportation sectors, the international maritime activity accounted for approximately 843 Mt of CO_2 or 3 % of global CO_2 emissions from fuel combustion in 2007. The International Maritime Organization forecasted that CO_2 emissions from international maritime activity are expected to rise by 10-26% by 2020 and by 126-218 % by 2050. A considerable increase is expected also for the air traffic: the IEA (International Energy Agency) estimated that international aviation emitted 397 Mt of CO₂ in 2006, plus 332 Mt CO₂ for domestic aviation. From 1990 to 2006, emissions from international air travel and freight have increased 55 % or at an average yearly rate of 2.8 % and it has accelerated in recent years (4.1%/year from 2002). An important factor to consider is that aircrafts emit CO₂ and shorter-lived greenhouse gases and particles directly into the upper troposphere and lower stratospheres, where they have an impact on atmospheric composition. The short-term warming impact of the sum of these emissions can be as high as twice the long term CO₂ impact alone [5,20,21].

The European union (EU) climate and energy policy is committed with a set of binding legislations which aim to meet ambitious targets for 2020. These targets, also known as 20-20-20 targets, set three key objectives [22]:

- 20 % reduction of CO₂ emissions from 1990.
- Rise the energy produced from renewable resources to 20 %
- 20 % improvement in the energy efficiency

In light of the previous considerations, it is clear then that the study of a process that would allow the increase of efficiency in petrol derived fuels utilisation and a reduction of the greenhouse emissions is of primary interest for the European and worldwide energy plans.

In the short-term only a few alternative fuels for the transportation sector are likely to be cost-competitive with gasoline or diesel; essentially sugar cane ethanol and very large coal-to-liquid plants. The latter, without yet-to-be-developed carbon capture and storage technology, would lead to more CO_2 emissions than the fuels it would replace. Improvements in traditional and hybridised internal combustion engine technology will continue to be the greatest source of GHG reduction from vehicles in the short-medium term. Electrification of mobility will play a growing role over the longer term, though hurdles relating to battery costs, vehicle range and energy distribution will need to be overcome. Fuel-cells transports, using hydrogen as energy vector, represent an interesting long-term driving technology, but costs are currently projected to be higher than for battery electric transports and in order to make this technology viable still many improvements need to be achieved [20].

From an economical point of view the gradual switch to fuel-cell electrical vehicles, either alimented with an on-board hydrogen generation system or with the assistance of a hydrogen storage technology, will change magnitude of the request for hydrogen supply [4]. At the moment the global annual hydrogen production is over 50 million tons and the consumption is increasing of about 6 % per year. The main utilization is in industrial processes: ammonia synthesis consumes around the 53 %, while petrol refining processes (hydrotreating and hydrocracking) around 20 % [10,23]. From data collected by a market study of 2010, hydrogen production market in terms of value was estimated to be 82.6 billion dollars [24]. With the prospective of using H_2 as energy vector the demand on the market is doomed to increase drastically for the sectors of transportation and energy generation. This perspective already launched an economic growth of this sector with the building of new production plants and financing the scientific research and development (new materials for catalysis, storage and fuel-cell) [1,13,25]. The improvements achieved in the last years have already contributed to a diminution of production prizes and costs of the technologies and many projects aiming in the same direction are under development to make the hydrogen exploitation and fuel-cells technology economically competitive. A relevant study published in 2011 by the DOE (USA Department Of Energy) by the name "Hydrogen and fuel cells program plan" [2] had the objective to explore the techniques and costs for hydrogen production in the scenario of a H_2 based energy system. The perspective is a scenario where the H_2 production approach, with a variety of scales ranging from large, centralized production to small, local (distributed) production, will achieve a delivery untaxed cost in the range of 2 \$ to 4 \$ per gallon gasoline equivalent (gge). This range represents the values at which hydrogen is competitive with gasoline. The only technology currently inside this range is the steam

reforming of natural gas, while for other techniques that use renewable resources more progress have still to be made: water electrolysis and biomass gasification are respectively in the range of 7-10 \$/gge and 6-9 \$/gge depending on the production scale and, for the electrolysis, depending on the price of the electricity. The evolution of hydrogen delivery prices for different production techniques is shown in Fig. 5.



Figure 5 - Hydrogen production costs evolution [2]

Therefore the road towards an hydrogen based energy system is a longterm project which presents many difficulties in terms of infrastructures, distribution and maturity of the technologies for hydrogen production, storage and conversion into electricity with fuel-cells [9,26]. In the short-mid term the development of hybrid fuel-electric vehicles could be the thread connecting the current fossil fuels based transportation system to a future hydrogen based one.

1.3 On-board hydrogen supplying

The development of fuel-cell vehicles is facing the big barrier of onboard hydrogen supply [25] due to its gaseous property and low density at standard conditions. The cruising range of vehicle is limited by the amount of hydrogen on-board and fuel-cell vehicle's high efficiency can only compensate for part of this disadvantage. In order to supply the required hydrogen to the vehicle's fuel-cells there are two possibilities: the utilisation of an on-board hydrogen storage system or the direct on-board hydrogen generation.

1.3.1 On-board hydrogen storage

The leading technology to store hydrogen is in the high compressed gaseous form (CGH₂). Steel tanks or lightweight composite tanks designed to endure very high pressures are becoming more and more common in prototypes vehicles. Cryogas, gaseous hydrogen cooled to near cryogenic temperatures, is another alternative that can be used to increase the volumetric energy density of gaseous hydrogen.

 CGH_2 is the current leading technology for hydrogen storage, but there are still many issues for the application on-board vehicles: hydrogen capacity depends on the tank volume and pressure. The higher is the pressure, the thicker has to be the tank wall for mechanical resistance with a related weight increase. Also, for mechanical resistance reasons, the tank cannot be shaped as a vehicle trunk to optimise the spacing, but it has to be cylindrical. At last the energy required for hydrogen compression must be considered: the higher is the concentration in the tank the higher is the energy required to compress the gas. Even though CGH_2 is the closest, it still doesn't fulfill all the milestones identified by the IEA and U.S. DOE for on-board hydrogen storage technologies [6,8,14,15,19,27,28]. The second most common way to store hydrogen is in the form of cryogenic liquid (LH₂). This technology has the advantage of a great volumetric and gravimetric hydrogen capacity, but is still less efficient and more expensive than CGH₂ because of the hydrogen liquefaction energy, evaporative losses, boil-off losses and the considerable thickness of the tank needed for the thermal insulation [6,8,14,19,27,28]. The last possible method for on-board hydrogen storage is the chemical storage: chemical compounds containing a high amount of H₂ can be used to deliver the hydrogen on the condition that the energy needed for the hydrogen release is not excessive. Many compounds have been studied: metal hydrides (AlH₃, NaBH₄,), amine-borane compounds (BH₃NH₃, NH₃B₃H₇), amides and imides. This is the most recent hydrogen storage technology and, even if the margin of improvement is big, currently the limitations for an on-board application are still too prominent: material density changes during operations and charge/discharge energy for the hydrogen. Also chemical hydrides storage is the farthest from IEA and DOE specifications in terms of H₂ gravimetric capacity and recharge time [6,8,14,15,19,27,28]. In Fig. 6 is shown a ranking of the hydrogen storage techniques in terms of gravimetric and volumetric capacity:



Figure 6 - Ranking of hydrogen storage techniques in terms of gravimetric and volumetric capacity [12]

In Table 1 are reported some of the milestones identified by the U.S. DOE for the development of storage systems in fuel-cell electric vehicles in the near future:

Storage parameter	Units	2010	2015	Ultimate target
	kWh∙kg⁻¹	1.5	1.8	2.5
Gravimetric density	MJ·kg⁻¹	5.4	6.5	9
	H_2 % wt.	4.5	5.5	7.5
	kWh∙L ⁻¹	0.9	1.3	2.3
Volumetric density	MJ⋅m ⁻³	3.2	4.7	8.3
	gH₂·L⁻¹	28	40	70
Fuel cost at pump	\$∙gge ⁻¹	3-7	2-6	2-3
System filling time	min	4.2	3.3	2.5
for 5 kg H ₂				
Maximum H ₂ losses	g·(h·kg _{H2} ⁻¹)	0.1	0.05	0.05

Table 1 - U.S. DOE milestones for fuel-cell electric vehicles storage system [15,28]

Observing Table 1 it is possible to see that considerable improvements are expected from the hydrogen storage technologies, achieving in the future an acceptable praticity, capacity and cost; but currently the characteristics of the storage systems are insufficient to make fuel-cells vehicles competitive with the present technology.

1.3.2 On-board hydrogen generation

1.3.2.1 Reforming techniques

An alternative for hydrogen supply is to generate on-board the hydrogen required by the vehicle, providing a solution to the technical and safety problems of storing large amounts of hydrogen. Nowadays, the majority of the H_2 produced come from fossil fuels (more than 90 %) and the main method of production is the steam reforming of natural gas from which around 50 % of hydrogen is obtained [10]. The three principal process for hydrogen production from fossil fuels are steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR). These technologies produce a hydrogen rich gas which contains also a great amount of carbon monoxide. Thus, in a subsequent step, one or more chemical reactors are used to convert CO into CO₂ and H_2 via the water-gas shift (WGS) increasing further the hydrogen yield. Depending on the catalyst sulfur resistance the fossil fuel may need to be pre-treated in order to eliminate sulfur compounds that can cause the deactivation. The reaction equations related to this processes, describing the conversion of a generic hydrocarbon to hydrogen, are here reported:

> Steam reforming

$$C_n H_m + n H_2 0 \leftrightarrow n C 0 + (n + \frac{m}{2}) H_2$$

Partial oxidation

$$C_n H_m + \frac{n}{2}O_2 \leftrightarrow nCO + \frac{m}{2}H_2$$

Auto-thermal reforming

$$C_n H_m + nH_2 O \leftrightarrow nCO + (n + \frac{m}{2})H_2$$

 $C_n H_m + \frac{n}{2}O_2 \leftrightarrow nCO + \frac{m}{2}H_2$

> Water gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

In the steam reforming (SR) the fuel is introduced in the reforming reactor together with water vapour to form a hydrogen rich gas. Ni based catalysts are the more common material used in the process. This reaction is endothermic so a certain amount of heat is needed in order to keep a correct reaction temperature (500-1000 °C). The SR process is normally used for the conversion of light hydrocarbons (HCs) like methane and natural gas [8,19,29,30].

The partial oxidation (POX) is a process generally used for the conversion of heavier hydrocarbons. The reaction takes place with a substoichiometric mixture of air and fuel that is partially combusted in a reactor. This is an exothermic reaction that is carried out at high temperature (1100-1500 °C). The catalysts used in this reaction usually consist in platinum or chromium oxide supported on silica [8,19,29,30].

Auto-thermal reforming (ATR) is a process that combines the advantages of both SR and POX: the exothermicity of the POX reaction is used to balance the endothermicity of the SR reaction. The two reactions are carried out simultaneously and if the steam/fuel and oxygen/fuel ratios are properly adjusted, no additional external energy is needed to run the process. The ATR process commonly operates between 950-1100 °C [8,19,29,30]. A simplified scheme valid for SR, POX and ATR process is reported in Fig. 7.



Figure 7 - Block diagram for hydrocarbon SR, POX and ATR

The exploitation of SR, POX or ATR reaction for on-board hydrogen generation would avoid all the problems connected to the on-board hydrogen storage. On the other side there are many other problems emerging for those processes:

- Required additional unit for fuel desulfuration (SR, POX, ATR)
- Required water vapour supply for the reaction (SR, ATR)
- Required heat exchange unit for cooling and safety (POX)
- Required additional WGS reactor to achieve a good process efficiency (SR, POX, ATR)
- Required additional purification unit for CO elimination (SR, POX, ATR)

These limitations make difficult the practical application of SR, POX and ATR process on-board a vehicle in terms of spacing and weight. The need of

additional units as a desulfuration unit for the pre-treatment of the fuel, an additional reactor for the WGS and a purification unit for the elimination of CO cause a drastic increase in the weight and dimension of such systems. Beside that the purification unit must be very efficient because fuel-cells, especially PEM-FC, are easily poisoned by even small amounts of carbon monoxide [8,19,21,29,30].

Recently another fuel processing technology is gathering growing interest for hydrogen delivery purposes: the dehydrogenation of liquid hydrocarbons. This technique allows the production of high purity, CO free hydrogen, without denaturating the starting hydrocarbons which can be reused for useful purposes. The principles at the base of hydrocarbons dehydrogenation process are explained in detail in the following chapter (1.3.2.2).

1.3.2.2 Hydrocarbons dehydrogenation

Hydrocarbons provide several advantages for hydrogen delivery purposes, such as relatively high hydrogen capacity on both the weight and volume basis (generally over 5 wt % and 50 g L^{-1}). The use of a catalytic dehydrogenation reaction of a hydrocarbon (the most studied are cycloalkanes such as methylcyclohexane, cyclohexane and decalin), coupled with the hydrogenation of corresponding aromatics is a promising process for hydrogen delivery and transportation. As cycloalkanes are in liquid phase at ambient conditions. their transportation can exploit the existing transport infrastructures (lorries, trains, boats...) and the wide presence of hydrogenation/dehydrogenation facilities would further diminish the investment costs for the actuation of such a hydrogen delivery system. Another huge advantage is that the hydrogen delivered with this method has a very high purity and it is CO and CO₂ free allowing the direct alimentation of fuel-cells. An example of hydrogen delivery via hydrocarbon dehydrogenation is showed in Fig. 8:



Figure 8 - Scheme for hydrogen delivery via hydrocarbon dehydrogenation

The literature regarding the dehydrogenation reaction is very rich and different catalysts with good activity have been identified, even though those studies are often targeted to the production of olefins as building block for the chemical industry. However there are also several studies involving dehydrogenation/hydrogenation of hydrocarbons as a method for hydrogen delivery and storage: Patil et al. [31] have carried out a study on Ni-Cu supported on activated carbon cloth (ACC) for methyl-cyclohexane, cyclohexane, decalin and piperidine dehydrogenation in a pulse spray reactor achieving good selectivity but poor conversions (10-20 % for mecyclohexane). There are some examples of dehydrogenation catalysts based on non-noble metals like Ag and Ni [32,33], but the conversion is pretty low and despite their lower cost, platinum is generally preferred for the hydrogen delivery purpose. In fact Pt is active even at lower temperature avoiding the cracking reactions and coke deposition that are favoured at high temperatures (> 500 °C) and lead to deactivation of Ni catalysts; this also favour the selectivity toward hydrogen and aromatic compounds without compromising the reversibility of the process. Usually platinum content in those catalysts varies between 0.1-3 wt % and is possible to use many porous materials as support: Al₂O₃, SiO₂, ACC, carbon black, carbon nanotubes and carbon nanofibres [16,18,34–38]. The most common process for the hydrocarbons

dehydrogenation is a heterogeneous gas-phase reaction carried out in a continuous fixed bed reactor (often a plug flow reactor), that operates in a temperature range of 300-500 °C. In Table 1 is reported a summary of the most recent and significant publications involving dehydrogenation catalyst for hydrogen delivery purpose. The concept of using hydrocarbons for hydrogen delivery, applied to complex mixtures of hydrocarbons and fuels, is explained in Chapter 1.4.

Ref.	Year	Active Metal	Support	Reagent	Phase
[31]	2013	Ni-Cu 1-10 wt%	ACC	Me-cyclohexane Decalin, Tetralin	Spray pulses
[32]	2012	AgM 5-10-15wt% (M=Pt, Pd, Rh)	ACC	Cyclohexane	Gas
[33]	2008	Ni 5-10-15-20 wt%	Al ₂ O ₃	Me-cyclohexane	Gas
[18]	2013	Pt 0.3-1 wt% PtRe 0.3 wt% PtPd 0.3 wt%	Al_2O_3	Me-cyclohexane	Gas
[35]	2011	Pt 0.1-1 wt%	СВ	Me-cyclohexane	Gas
[36]	2014	Pt 5 wt%	CNT, CNF, AC, Graphite	Decalin	Liquid (MW)
[38]	2014	Pt 1-5 wt%	CNF, CB, CXG, AC, OMC	Decalin	Spray pulses
[39]	2012	Pt 3 wt%	V ₂ O ₅ , Y ₂ O ₃	Me-cyclohexane	Gas
[40]	2010	Pt 3 wt%	Metal oxides (La, Zr, Ti, Ce, Fe, Al, Mn) Perovskites (La, Y)	Me-cyclohexane	Gas
[41]	2006	Pt 0.6 wt%+K 0.1 wt%	Al_2O_3	Me-cyclohexane	Gas
[17]	2008	Pt or Pd 1-5 wt%	Sibunit, AC, Al ₂ O ₃	Ter-cyclohexane	Liquid
[42]	2004	Pt or Pd 0,25-1 wt%	Stacked cone CNT	Me-cyclohexane Cyclohexane	Gas
[43]	2012	Pt	AC, Al ₂ O ₃	Decalin	Gas
[44]	2006	Ni-Raney	-	Me-cyclohexane	Bi-phase

Table 2 - Summary of catalysts for hydrogen delivery via dehydrogenation reaction

1.4 Fuels partial dehydrogenation

1.4.1 Principles of the fuel partial dehydrogenation

The idea of generating hydrogen via partial dehydrogenation (PDh) of fossil fuels on-board, derives from the concept of using hydrocarbons as hydrogen delivery media described in Chapter 1.3.2.2. The difference between the two processes is that in the hydrocarbons dehydrogenation, usually a pure cyclic hydrocarbon, is completely dehydrogenated to give the corresponding aromatic. The aromatics formed are stored and afterwards carried to a hydrogenation facility to close the cycle. PDh of fuel, is considered more as an hydrogen production process: the reaction is carried out on a complex mixture of hydrocarbons as kerosene, diesel, naphtha or gasoline and a fraction of the combustible contained in the vehicle tanks is partially dehydrogenated to produce the hydrogen required. Indeed through a controlled dehydrogenation, the properties of the dehydrogenated fuel are not expected to change considerably and it will still be appropriate for the use as propellant in the thermal engines. A patent describing this process has been deposited by Airbus [45]. The purpose of using fuel-cells instead of turbines or alternators for electricity generation is expected to increase the system efficiency and consequently optimising the fuel utilisation and decreasing the GHG emissions. A simplified scheme of the fuels PDh process is reported in Fig. 9.



Figure 9 - Scheme for the fuels PDh process

Beside the possibility of reusing the fuel after reaction, this new fuel processing technology present many advantages respect the reforming technologies for on-board hydrogen production. PDh system is more compact compared to the reformers as the hydrogen produced is expected to be almost pure and not containing CO. This avoid the necessity of a bulky purification unit that is required for the reforming processes. The products of the fuels PDh are expected to be only hydrogen and the dehydrogenated fuel; this is big advantage in comparison to the reforming processes which produce also big amounts of CO and CO₂. As consequence the PDh process doesn't require the additional water gas-shift reactor needed by reformers making it even more compact and convenient.

1.4.2 Theoretic evaluation of the process

The partial dehydrogenation of fuels is a complex process and it presents more difficulties respect the reaction on a single hydrocarbon. The main reason is the combined reactivity of all the classes of compound contained in the mixture: beside the simple dehydrogenation of paraffins to olefins and cyclic to aromatics, there are many different reaction pathways. The formation of intermediate products that can react with each other via condensations or polymerisations leading to carbon coke formation and also the presence of undesired reactions like cracking and hydrocracking make hard to predict the efficiency and the products of this type of reaction. Bashin et. al. [46] performed a detailed study on the reaction of paraffin dehydrogenation to olefins explaining all the possible alternative pathways observed on acidic sites and Pt metal sites. In Fig. 10 a scheme representing the reactivity of long chain paraffins (C_{10} - C_{14}) is shown:



Figure 10 - Reaction mechanisms by platinum and acid sites in heavy paraffins dehydrogenation [46]

Depending on the reaction conditions and the acidity, different cracking products can be formed, leading also to the formation of lighter paraffins that can continue the reaction path as illustrated in Fig. 11:



Figure 11 - Reaction mechanisms by platinum and acid sites in light paraffins dehydrogenation [46]

The main difference is that light paraffins (C_2-C_5) cannot form cyclic hydrocarbons via dehydrocyclisation, simplifying the reaction pathway respect the heavier paraffins.

The other main class of compound that is reactive in dehydrogenation conditions is the cyclic hydrocarbons class. The dehydrogenation of a cyclic hydrocarbon (ex. cyclic C_6) is in general thermodynamically more favoured than the dehydrogenation of the corresponding paraffin (ex. n- C_6) because of the formation of a stable aromatic ring, therefore it is expectable that during the dehydrogenation of a complex mixture of hydrocarbons the cyclic compounds will display the highest conversion values. The scheme showed in Fig. 12, based on a study carried out by Alhumaidan et. al. [18], represents the reactivity of cyclic hydrocarbons for dehydrogenation reaction on supported Pt catalysts. The model molecule considered is methyl-cyclohexane:



Figure 12 - Reaction mechanisms by platinum and acid sites in cyclic hydrocarbons dehydrogenation [18]

The aromatics class of compounds is not expected to be very reactive under the dehydrogenation condition, although metal and acid sites could catalyse some undesired reactions like demethylation, condensation or disproportionation. The condensation reaction is one of the main pathways to the formation of the precursors of a highly ordered coke, that causes the catalyst deactivation. A scheme representing these pathways for aromatics is shown in Fig. 13. The model molecule considered is toluene:



Figure 13 - Reactivity of aromatics on platinum and acid sites under dehydrogenation conditions [18]

The partial dehydrogenation of fuels is therefore a difficult process to control because all this different pathways that can either contribute to hydrogen production or lead to the catalyst deactivation. A further limitation related to the composition of fuel is the possible presence of sulfur containing compounds and additives [47]. Apart from the fuels synthesised by Fisher-Tropsch reaction [48], the ones obtained by oil fractionation contains a certain amount of sulfured compounds which can cause the dehydrogenation catalyst poisoning [49]. Commercial fuels also contain a range of additives like antioxidant, metal blockers, static dissipaters, corrosion inhibitors, icing inhibitors and biocides. The effect of these additives on the PDh catalytic process is still unknown and be considered in this work during the study on commercial fuels.

Theoretically it is possible to generate a high amount of hydrogen from fossil fuels via partial dehydrogenation; the key factors are to optimise the process conditions and the catalyst properties in order to achieve a good compromise between activity and stability. The catalyst for this process must be sufficiently active at low temperature (in the range 300-500 °C) in order to minimise the cracking reactions and it should be sulfur resistant. The operating pressure value must be a compromise between the hydrogen production (thermodinamically favoured at low pressure) and the pressurization necessities for a practical application. The acid sites content and distribution also have to be controlled in order to avoid undesired reactions (ex. polycondensation) [18,46].

The very first reported example of fuel partial dehydrogenation, in which kerosene is used as reagent, is from Wang et. al. [50] in 2008. The group performed a study using Pt/ γ -Al₂O₃, Pt-Sn/ γ -Al₂O₃ and Pt/ γ -Al₂O₃-ZrO₂/SO₄⁻² as catalysts for the dehydrogenation of Jet-A1. The reaction was carried out in diluted conditions (67 % vol. N₂ in the feed) and with a hydrogen recycle (17 % vol.), achieving a hydrogen yield in the range of 4-12 % depending on the catalyst and the conditions. This study also highlights a very quick deactivation already in the first two hours of reaction probably due to the sulfur poisoning and to the acidic properties of the material tested that produced high quantity of coke in course of reaction [50].

The catalytic partial dehydrogenation of fuels for on-board hydrogen generation is a very recent fuel processing technology and it began to attract increasing interest since the studies carried out during the European project "GreenAir", with a boost in the number of scientific publications [51–56]. Similarly to the example just mentioned the fuel considered is kerosene for aviation applications. A description of the funding ideas of the project as well as the objectives and targets are reported in Chapter 1.4.3.

1.4.3 The partial dehydrogenation of kerosene: "GreenAir" project

The "GreenAir" project, inside which this thesis project started, had the objective to study a technology for reducing the pollution of the aviation traffic in the direction of the engineering of a "more electric aircraft" (MEA). This European project, started in 2009 and funded by the European Seventh Framework Program for transports (FP7 transport, grant agreement n°233862) gave birth to an international collaboration between thirteen industries, universities and research institutes (Airbus, CESA, CNR, CNRS, DLR, EADS, Efceco, HyGear, ITLSR, Johnson Matthey, Quinetic, University of Montpellier 2 and University of Bologna) for a total investment of approximately 8 million Euros. This collaboration aimed at the implementation of a fuel-cell system on-board the plane to achieve a more efficient and cleaner electric power generation. Current conventional aircrafts need different types of power (hydraulic, pneumatic, electric...) that are provided by the main engines and auxiliary power unit (APU). In an optimized MEA pneumatic, hydraulic and mechanic devices are replaced by more efficient electric ones and the main engines are optimized for propulsion only thus reducing the fuel consumption and electric power required. As first step towards MEA is then fundamental to investigate the possibility of replacing the traditional APU with a fuel-cells secondary power generation unit. In order to supply the fuel-cells with the required hydrogen while on-board the aircraft the "GreenAir" project partners investigated the possibility of direct on-board generation of hydrogen using as source the kerosene Jet A-1 in the plane tanks.

On-board generation is feasible if the process can deliver a sufficient amount of hydrogen in a relatively compact, light-weight and "green" way. Current methods of hydrogen generation from hydrocarbon, as steam reforming, partial oxidation and auto-thermal reforming, do not fulfill those criteria: the purity of the hydrogen generated is low so the gas mixture needs a bulky purification unit (WGS reaction and pressure swing adsorption) to eliminate the considerable amount of CO and CO₂ produced in those processes and achieve a sufficient purity for a PEM fuel-cell system alimentation; this would make those option impossible to be applied on-board any aircraft.

In principle it is possible to use standard Jet A-1 kerosene to power an on-board fuel-cell system via partial dehydrogenation, without the need to have hydrogen tanks or to certify the dehydrogenated kerosene produced. The advantages of this method are the H₂ high purity, the absence of CO/CO₂ and the possibility of reusing the dehydrogenated kerosene for useful purposes. By these preliminary considerations the choice for the project was to study the feasibility of a catalytic partial dehydrogenation (PDh) process for the hydrogen delivery to a PEM fuel-cell system. In the process only a small fraction of the hydrogen in the fuel is taken, sufficient to feed the fuel-cells and generate the required amount of electricity. The dehydrogenated kerosene properties should not change considerably and after mixing with the original fuel in the main tanks it will still be under the specification for Jet A-1. This would allow using the reaction product as combustible in the main engines.


Figure 14 - Scheme of an airplane with fuel-cells alimented by a PDh reactor

The minimum net heat of combustion for kerosene Jet A and Jet A-1 to be certified as jet fuel is 42.8 $MJ \cdot kg^{-1}$. The range of net heat of combustion found for various commercial jet fuel is 42.8 - 43.5 $MJ \cdot kg^{-1}$ and from this values is possible to calculate the hydrogen yield achievable by partial dehydrogenation [21].

 Table 3 - Potential hydrogen yield as function of net heat of combustion of the kerosene [21]

Heat of Combustion (MJ·kg ⁻¹)	42,8	43,0	43,2	43,5
Hydrogen content (% wt)	12,97	13,34	13,71	14,28
Hydrogen Yield (% wt)	0	0,37	0,74	1,31

This estimation considers the maximum yield of hydrogen possible if is considered to dehydrogenate equally the total amount of kerosene contained in an airplane fuel tank. Considering a fuel flow of 6 ton \cdot h⁻¹ (average consumption of an Airbus A340) with a net heat of combustion of 43.2 MJ·kg⁻¹, hydrogen energy density of 33.3 kWh·kg⁻¹ and 50 % PEM-FC

efficiency it would be theoretically possible to generate 739.62 kWh of electricity. This estimation is made to display the high potential of the project; in the practice the aim would not be to dehydrogenate the total amount of kerosene in the tanks with the minimum yield, but to carry out the reaction on a fraction of the kerosene with the required yield to feed the FC and then mix it with the original Jet A-1 before the combustion to keep a proper net heat of combustion.

The investigation on PDh of kerosene is required to achieve various technical milestones, some related to the catalysis part and some to the system engineering, in order to prove the feasibility of such a system for on-board electricity supply. In Table 4 are reported the objective and the minimum values to reach in the first phase of the research in order to continue the investigation on a larger scale system [21] (laboratory prototype for on-board PDh).

PARAMETERS	TARGET
System efficiency (%)	50
H_2 production (NL·h ⁻¹ ·kg _{cat} ⁻¹)	1000
Electric Power (kWe)	1
Lifetime (h)	100
H ₂ purity (% vol.)	> 95
Sulfur tolerance (ppmw)	300
Start-up time (min)	< 15
Dehydrogenated fuel combustion energy (MJ·kg ⁻¹)	42.80

Table 4 - Technological milestones for the "GreenAir" project

The preliminary tests for the project were performed in laboratory scale reactor with a fixed catalytic bed, using as catalysts Pd based catalysts supported on hydrotalcite and Pt based catalyst supported on alumina. The most promising emerged to be the Pt/alumina materials so the early stage studies focused mainly on this type of catalyst. As reported by Resini et. al. [51], 5 % wt. Pt-1 % wt. Sn/ γ -Al₂O₃ and 5 % wt.Pt-1 % wt. Sn-1 % wt. Na/ γ -Al₂O₃, prepared by successive impregnations of the metals precursors on γ -Al₂O₃ preformed pellets (Degussa), then dried and calcined in air at 500 °C, were tested at 350 °C - 5 bar showing the possibility of producing quite high purity H₂ (90-96 %) containing mainly impurities of CH₄ and light hydrocarbons, but with performances that are still far away from the project minimum target: with normal Jet A-1 kerosene the lifetime is in the order of few hours) but the productivity is very low (less than 300 NL·h⁻¹·kg_{cat}⁻¹).

After those preliminary studies the optimisation of the material and conditions was made using as a kerosene surrogate, composed by five different hydrocarbons, in order to have a better comprehension of the reactivity for the different classes of hydrocarbons and to focus on the carbon deposition deactivation without considering the sulfur problem. During my master degree internship at the University of Bologna, as reported by Lucarelli et. al [55], the optimal Pt-Sn ratio for γ -Al₂O₃ supported catalysts has been researched. The amount of 1% wt. Pt-1% wt. Sn, incorporated on the alumina support via successive impregnations of the two metal precursor solutions, has been identified as the optimal amount. This material, labelled JM1, has been tested under different operative conditions identifying as the best parameters T = 450 °C, P = 0.5 MPa, 7 % vol. of hydrogen recycle and 2 s contact time (calculated at STP).

The first tests results indicates therefore the 1 % Pt-1 % Sn/γ -Al₂O₃ catalytic system as a promising option for the partial dehydrogenation of kerosene. The best operative condition to carry out this gas-phase catalytic reaction seems to be around 450 °C for the temperature and around 2 seconds in terms of contact time; the pressure is kept at 1 MPa for a choice connected to the final application in the project. Taillades-Jacquin et. al. [56] performed an investigation on the acidity effect on the PDh of low sulfur kerosene (LSK) using as catalyst supported Pt-Sn impregnated on a series of modified γ -Al₂O₃: the introduction of additives in the support structure modify the surface acidity

leading to an increase of the catalyst stability. The best material displayed an average hydrogen productivity of 1800 NL·h⁻¹·kg_{cat}⁻¹ during the 4 h TOS, but the deactivation is still considerable. A further study by Lucarelli et. al. [54] has been performed using Pt-Sn/y-Al₂O₃ and Pt-Sn-K/y-Al₂O₃ using as reagent two surrogate mixtures compared to a LSK fuel in order to investigate the deactivation via carbon coke deposition. The best performance observed feeding a real kerosene LSK is obtained with Pt-Sn-K/ γ -Al₂O₃ display an average hydrogen productivity of 1400 NL·h⁻¹·kg_{cat}⁻¹ during a 18 h TOS with an extrapolated lifetime of 42,5 h. A mechanism leading to carbon coke formation via polymerisation and polycondensation has been hypothesised and the possibility of regenerating the catalyst has been verified via oxidation in air flow at a T = 425-550 °C. Starting from these considerations during the thesis project different studies on material and process have been carried out in order to further improve the performances of kerosene partial dehydrogenation.

1.4.4 Gasoline and diesel partial dehydrogenation

Partial dehydrogenation of petrol fractions other than kerosene has currently never been performed. No reports of this kind of reaction have been found in the literature. The studies on kerosene derive from the founding idea of the "GreenAir" project of building a fuel-cells based APU for the electricity generation on-board airplanes, therefore the application to other vehicles involve an investigation about the possibility of adapting the process to other kind of fuels. As first step a study of the feasibility of a process based on gasoline or diesel partial dehydrogenation is of primal interest.

Kerosene is a petrol fraction that is mainly used for aviation applications and has a boiling point that is intermediate between diesel and gasoline. The most common petrol fractions used as combustible in naval and road transportation are diesel and gasoline. The first one is heavier than kerosene, it contains usually a range of hydrocarbons with distribution centred on C_{16} , while gasoline has lighter hydrocarbons with a distribution around C_8 [57,58]. The different composition of these two fuels respect the kerosene, together with the different amount of sulfur containing compounds, will probably change the reactivity and the optimal parameter for the catalytic partial dehydrogenation reaction. A pioneering study, finalised to assess the feasibility of the process, consisting in preliminary studies on gasoline and diesel fuels partial dehydrogenation, will be presented in this thesis manuscript (Chapter 3).



Figure 15 - Application of PDh fuel processing technology on road transportation

1.5 References

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2. Hydrogen generation via partial dehydrogenation of kerosene

There is an on-going effort in the aeronautic industry to achieve more efficient and cleaner power generation aiming at a "greener" aircraft architecture. One option to reach this objective is the on-board electric power generation by a separate autonomous unit and fuel-cells are the most appropriate candidates to fulfil this role. The hydrogen produced will be used to feed a PEM fuel-cell system that substitute the classic turbine auxiliary power unit (APU) of the plane. As previously explained in Chapter 1.4.3, the choice of the catalyst for this process is crucial because it should allow producing high purity hydrogen without compromising the original properties of kerosene. The literature on the dehydrogenation of hydrocarbons, to produce high purity hydrogen, suggests that the best catalysts for this reaction are based on Pt supported on high surface area porous materials. There are many properties of the catalyst that can influence its performance and durability: they can be properties characteristic of either the active phase or the support, or a combination of both. It has been observed that the first cause of deactivation is the deposition of carbon coke on the catalyst; this is correlated to the catalyst acidity, the porosity, the metal activity and dispersion. The presence of strong acid sites is known to catalyse cracking reactions that lead to the formation of coke precursors [1,2]. The pore size and shape of the support is also very important, as it is reported that one of the possible mechanism of deactivation by coke deposition is the pore plugging that impedes the reactants access to the active sites, therefore causing a loss of activity [3]. The intrinsic activity of the active metal towards the dehydrogenation reaction can affect the rate of carbon coke formation: if the activity is too high, the deep dehydrogenation can lead to the formation of dienes which via polymerisation and polycondensation results in carbon coke formation. Often in the case of Pt based catalysts, a second metal (ex. Sn, Zn) is added in order to modulate the Pt activity and achieve a better stability [4]. The metallic dispersion is also important: in the case of Pt based catalyst [5], for example it is known that large nanoparticles are more likely to catalyse hydrocracking reactions that lead to formation of coke precursors [3].

2.1 Description of the catalytic materials used in this study

In the partial dehydrogenation work package of the "GreenAir" project it was concluded that one catalyst with the higher activity in the partial dehydrogenation reaction of kerosene is a combination of Pt and Sn with an optimal ratio between the metals of 1:1 (in weight) [6,7]. As a consequence, in this work, a Pt-Sn/ γ -Al₂O₃ has been chosen as reference catalyst to which a range of materials are compared and studied.

2.1.1 Baseline catalytic materials

> Catalytic materials prepared at Johnson Matthey

The materials utilised in the course of the "GreenAir" project, are here named JM1 and JM2. JM1 is the reference catalyst containing 1 % Pt-1 % Sn supported on a commercial γ -alumina. JM2 is a second generation baseline catalyst resulting in a modification of the JM1 reference material; the catalyst Pt-Sn (1:1) is supported on a BaO modified γ -alumina. JM1 and JM2 were via incipient wetness impregnation (IWI) of the support. JM materials in form of powder were shaped in pellets of 0.85-1 mm diameter for catalytic testing.

> UOP baseline catalytic materials

The materials named UOP1 and UOP2, obtained from UOP, are two commercial reforming catalysts. The support is γ -alumina shaped in the form of spheres of 1.5 mm average diameter; the unknown active phase has been incorporated on the support via impregnation.

		-
Name	Active Phase	Support
JM1	1% Pt, 1% Sn	γ -Al ₂ O ₃
JM2	1% Pt, 1% Sn	3% BaO γ-Al ₂ O ₃
UOP1	Pt	γ -Al ₂ O ₃
UOP2	Pt, Pd	γ -Al ₂ O ₃

The name, composition, and the nature of the support used are summarised in Table 1:

Table 1- Reference and baseline catalysts

2.1.2 Preparation of catalytic materials

The technique chosen for the deposition of the metals is the incipient wetness impregnation (IWI) with water solutions containing the metal precursors.

> Deposition of Pt/Sn on alternative supports

In order to evaluate the effect of the support, a series of catalysts containing equal amounts of Pt-Sn (1% wt. Pt 1% wt. Sn) has been prepared using various supports: two montmorillonites (MM1, MM2), two zeolites (USY, YNa), an ex-hydrotalcite (HT1) and two modified mesoporous silicas (SBA1, SBA2). The MM1 and MM2 supports are commercial Süd-Chemie montmorillonite clays obtained by acid activation with HCl at variable concentration and thermal treatment. K-10 and K-30 montmorillonites usually have values of surface area of 240 m²·g⁻¹ and 230 m²·g⁻¹ and they possess both Bronsted and Lewis acid sites [8,9]. The USY and YNa are zeolite type materials. Zeolites are microporous silicoaluminates with a regular pore structure. Due to their acidic properties, ion exchange capacity and their high

surface area are often used as molecular sieves or catalysts [10,11]. The HT1 material is a mixture of basic MgO and AlO from Prolabin-Tefarm s.r.l., obtained from the thermal treatment of the hydrotalcite. This type of materials exhibit properties such as large surface area, high thermal stability and basic character which make them suitable as catalysts for various processes [12,13]. The SBA1 and SBA2 materials are surfactant templated mesoporous silicas with a very high surface area given by the use of the tri-block copolymer Pluronics C123, which have been discovered by Santa Barbara research team [14]. SBA1 and SBA2 have been provided from the University of Malaga (Spain) and have been prepared according to a modification of the methodology developed by Zhao et al. [15]. SBA1 have been modified with the introduction of CeO in the SiO₂ matrix (SiO₂/CeO/ZnO mol ratio 10:1) and SBA2 with the introduction of CeO and ZnO (SiO₂/CeO/ZnO mol ratio 10:1:1).

All support were previously calcined at 600°C and subsequently Pt and Sn were added by co-impregnation using the appropriate amount of aqueous solutions of H₂PtCl₆·6H₂O (*Alfa Aesar*) and SnCl₂·2H₂O (*Acros*), to give a ratio 1% wt. Pt and 1% wt. Sn (mol. ratio Pt/Sn = 0.61). The tin precursor was dissolved in 1M HCl and then mixed with the platinum salt solution upon which the solution turns red-brown due to the formation of a [PtCl₂(SnCl₃)₂]²⁻ complex. It is reported that the procedure of Pt-Sn co-impregnation leads to a higher amount of Pt_xSn alloy formation than a catalyst obtained with successive impregnations, which tend to produce a mixture of Pt-Sn alloys, pure Pt and SnO₂ [16,17]. After drying the impregnated materials overnight at 80 °C, they were thermally treated in air at 120 °C for 2 hours and then at 560 °C for 2 hours (heating rate 2 °C min⁻¹).

> Deposition of Pt/Sn and Indium on alumina

In order to further improve the performance of the Pt-Sn bimetallic active phase, the effect of the addition of a third metal has been studied. It has already been observed that the addition of a third metal to Pt-Sn catalysts can lead to improvement of the catalytic properties, and examples of enhanced trimetallic catalysts for reforming or dehydrogenation can be easily found in the literature (ex. Pt-Sn-M/Al₂O₃ M=Re, Ir, Ge, In) [18–24]. There are some examples showing that indium addition remarkably enhances the catalyst stability and inhibits undesired hydrogenolysis reactions [22,25–27]. For this reason the third metal chosen is for the study is indium. A series of catalysts containing equal amounts of Pt-Sn (1% Pt, 1% Sn w/w) and a range of In contents (0%, 0.25%, 0.5%, 0.75%, 1% w/w) has been prepared by the incipient wetness impregnation technique, using as support a commercial γ -Al₂O₃ (Sasol Puralox SCFa40). Indium was added using aqueous solutions of differing InCl₃ concentration (Alfa Aesar), followed by drying at 80 °C. Subsequently Pt and Sn were added to the In/Al₂O₃ following the same method and precursors as described previously. After drying overnight at 80 °C, they were thermally treated in air at 120 °C for 2 hours and then at 560 °C for 2 hours (heating rate 2 °C min⁻¹).

The catalysts obtained by this method were labelled as "Cat-In[x]" where x is the percentage in weight of indium. A summary of the materials composition can be found in Table 3:

Name	Pt % wt	Sn % wt	In % wt
Cat-In[0]	1	1	0
Cat-In[0.25]	1	1	0.25
Cat-In[0.5]	1	1	0.5
Cat-In[0.75]	1	1	0.75
Cat-In[1]	1	1	1



> Deposition of Pt/Sn on sucrose templated alumina

The porosity of the support is a very important factor influencing the performance of the catalytic material and its stability. New alumina supports with enhanced porosity properties has been synthesised modifying the synthesis described by Xu et al. [28]. This new supports have been obtained using sugar as template: a water solution of $AlCl_3 \cdot 6H_2O$ (*Sigma–Aldrich*) was prepared and sucrose (*Sigma–Aldrich*) was then added with a molar ratio Al:sugar:H₂O 1:1:75 or 1:0.5:75. An aqueous solution of NH₃ (30% wt.) was added drop-wise to adjust the pH to 5 while stirring at 500 rpm. The resulting gel was heated at 60 °C until dry and calcined at 600 °C for 6 h, using a ramp rate of 2 °C min⁻¹. The resulting material obtained was labelled ALUSUC. A scheme of the new support synthesis is shown in Fig. 1.



Figure 1 - ALUSUC and ALUGLU synthesis scheme

Once the support is obtained, platinum and tin were added by IWI in the amounts of 1% wt. Pt and 1% wt. Sn following a similar methodology and thermal treatment as for the previous materials to obtain the catalysts labelled ALUSUC1[PtSn] and ALUSUC2[PtSn].

Table 3 - Composition of catalysts on sucrose templated alumina

Name	Ratio Al:sugar	Pt % wt	Sn % wt
ALUSUC1[PtSn]	1:1	1	1
ALUSUC2[PtSn]	1:0.5	1	1

2.2 Characterisation of the catalysts

The description of the techniques and the instrumentations used for the characterisation of the materials is reported in this chapter.

> X-ray diffraction

The X-ray diffraction (XRD) method of characterisation is based on the measurement of interferences of X-ray monochromatic beams thought the atomic planes in crystalline substances. These interferences must obey the Bragg's Law:

$2dsin\theta = n\lambda$

d = distance between crystalline planes n = entire number represents the diffraction order $\lambda =$ X-rays source wavelength

 θ = X-rays incidence angle

Changing the incidence angle of the X-rays source and collecting the signal of the diffracted beams, the sample diffractograms were registered. This technique allows us to identify the different crystalline species present on the surface of the sample. Each crystalline species has characteristic diffraction lines, making the X-Ray diffraction a fingerprint technique.

The instrument used for X-Ray diffraction (XRD) analysis was a *PANalytical X'Pert* diffractometer, with $CuK_{\alpha 1}$ as radiation source (λ =0.15418 nm, 40 kV, 25 mA); the acquisition time was 60 minutes. Phase identification was performed using *HighScore* software by *PANalytical*.

> X-ray fluorescence

The X-ray fluorescence (XRF) analysis is based on the measurements of the radiation emitted from excited atoms irradiated with X-rays. The radiation emitted, has energy that is characteristic of the atoms present. The term fluorescence is applied to phenomena in which the absorption of radiation of a specific energy results in the re-emission of radiation of a different wavelength. Chemical composition verification of the samples via XRF was performed using a *PANalytical AXIOS MAX* instrument, with a Rh radiation source (4 kW). Tablets of samples of 1.3 mm diameter and 1 mm thickness were used for the experiments. Elemental quantification was performed using *SUPER-Q* software.

> Nitrogen adsorption-desorption isotherms

The surface area of the samples is obtained from the nitrogen adsorption isotherm using the Brunauer, Emmett y Teller (BET) equation. This method is based on the original work of Langmuir but with an extension of the monolayer model to a multilayer adsorption model. The solid surface is considered as a distribution of adsorption sites in dynamic equilibrium with the adsorbent, where the condensation rate of the molecules over empty sites is equal to the evaporation rate of the molecules over occupied sites. The dynamic equilibrium is described by the following equation:

$$\frac{P}{V(P_0 - P)} = \frac{1 + (C - 1)}{CV_m} \frac{P}{P_0}$$

P = equilibrium pressure

 P_0 = saturation pressure

V = gas volume adsorbed for gram of sample

 V_m = gas volume needed for monolayer cover of a gram of sample

C = constant

Pore size distribution and the average pore diameter, were calculated using the Barrett, Joyner and Halenda (BJH) method. This method is based in the Kelvin equation, usually written as:

$$\ln\left(\frac{P_*}{P_0}\right) = -\frac{2\gamma\nu\,\cos\theta}{RTr_m}$$

 $P_* = critical condensation pressure$

 P_0 = saturation pressure

 γ = fluid surface tension

v = molar volume of condensed adsorptive

R = ideal gas constant

T = temperature

 r_m = curvature radius of fluid meniscus

In order to determine the main textural parameters of a porous material, like specific surface area, pore volume and pore size distribution, nitrogen adsorption/desorption at -196 °C (77 K) were measured using automatic equipments *ASAP 2020* or Tristar both from *Micromeritics*. Before analysis, the samples were out-gassed at 200 °C for 8 h under a vacuum of 66.7 Pa. The analyses were performed on ≈ 0.1 g samples in the form of powder.

> Ammonia thermal programmed desorption

The acidity of the materials was studied by NH₃ thermal programmed desorption (NH₃-TPD), using an *Autochem 2910* automatic system from *Micromeritics*. Samples of 100 mg were placed in a U shaped quartz cell, heated at 500 °C in a air flow (30 ml·min⁻¹ and heating rate 5 °C·min⁻¹) for 1 hour, cooled to 350 °C in He flow (30 ml min⁻¹) and reduced in H₂ flow (30 ml·min⁻¹) for 2 hours then cooled to 100 °C in He flow (30 ml·min⁻¹). Then a

flow of 30 ml·min⁻¹ pure NH₃ was passed through the samples for 1 hour, which were then flushed with He at 100 °C for 1 hour. NH₃ was thermally desorbed up to 600 °C with a heating ramp of 10 °C·min⁻¹ and the signal was registered using a TC detector.

This analysis allows a quantitative measurement of sample acidity and also a semi-quantitative distinction between the types of acid sites present. The strength of the acid sites is proportional to the temperature at which ammonia is desorpted and by comparison between samples it is possible to identify the prevalence of stronger or weaker acid sites. Desorption of ammonia at lower temperature is signal of the presence of weaker acid sites, while desorption at higher temperature signal the presence of stronger sites. The apparatus was calibrated using Ni(NH₃)₆Cl₂ as NH₃ source.

> Hydrogen thermal programmed reduction

H₂ thermal programmed reduction (H₂-TPR) was performed in an *Autochem 2910* apparatus. The sample of 100 mg was placed in a U shaped quartz cell, oxidised in synthetic air (30 ml·min⁻¹, 500 °C, 5 °C·min⁻¹), then after cooling to 50 °C, a flow of H₂ (5%)/N₂ mixture (30 ml·min⁻¹) was passed over the sample, which was then heated at 10 °C·min⁻¹ up to 700 °C, registering the H₂ consumption with a TC detector.

This technique measures the hydrogen uptake as function of the temperature giving useful information about the reducibility of the species present on the sample. By comparison with other samples and with the literature database it is also possible to have indications about the interaction between the species. In the present case the hydrogen uptake is related to the metal particles on the catalyst and the information obtained concern the interactions between the metals of the active phase and between the active phase and catalyst support.

> Hydrogen chemisorption

 H_2 pulse-chemisorption was performed in an *Autochem 2910* apparatus. The samples were heated in air flux (30 ml·min⁻¹; 500 °C, 5 °C·min⁻¹) and then reduced with a $H_2(5\%)/N_2$ mixture at 350 °C. Desorption of physisorbed hydrogen was carried out in N_2 flow at 380 °C for 1 hour. Pure H_2 pulses adsorption was recorded at 40 °C.

 H_2 static-chemisorption was performed in an *ASAP2020-CHEM* apparatus. The samples were heated in air flux (30 ml·min⁻¹, 500 °C, 5 °C·min⁻¹), purged in He flow at 200 °C, evacuated and then reduced with a H_2 at 350 °C. Subsequently the sample is evacuated again at 360 °C to eliminate the physisorbed H_2 and then the analysis starts. The stoichiometry assumed for the dispersion calculation was $Pt/H_2 = 2$ and for the particle size calculation the shape considered was a hemisphere.

The amount of chemisorbed hydrogen is determined from the isotherms branches in the case of the static-chemisorption and from the hydrogen pulse peaks for the pulsed-chemisorption. With this value, V_m , the number of accessible sites Ns can be calculated by the relationship:

$$N_s = \frac{V_m N_a F_s}{V_{mol}}$$

 N_s = number of accessible sites

 V_m = chemisorpted hydrogen volume

 V_{mol} = molar volume of the absorptive

 $N_a = Avogadro's$ number

 F_s = stoichiometry factor

The metallic dispersion can be calculated using the expression:

$$D(\%) = \frac{N_s}{N_t} \times 100$$

D(%) = dispersion percentage

 N_s = number of metallic accessible sites

 N_t = total number of metallic sites

> Mössbauer spectroscopy

This spectroscopic technique is based on the effect of recoil-free resonance absorption of quanta emitted, when a radionuclide decays to a stable daughter nucleus. The Mössbauer spectroscopy [29], also known as nuclear gamma resonance (NGR) spectroscopy, was discovered experimentally and explained theoretically by R.L. Mössbauer in 1957. This is a relatively sophisticated and sensitive technique yielding detailed information about the physicochemical state of atoms of selected elements. The high-energy resolution of this spectroscopic technique allows the detection of the interactions between the nucleus and the electrons in a solid, therefore permitting to obtain information about the chemical state. These are called hyperfine interactions:

• Isomer shift

The electric monopole interaction causes a shift of the resonance lines called isomer shift (δ): the interaction causing the isomer shift is part of the Coulomb interaction between the nuclear charge distribution of finite size and the negatively charged *S* electrons.

• Electric quadrupole splitting

The electric quadrupole interaction causes a splitting of the Mössbauer signal called electric quadrupole splitting (Δ): the interaction between the nuclear quadrupole moment (Q) and the electric field gradient (EFG) generated by the charge distribution of valence electrons and/or ligands in a chemical compound or, more generally, by the environment of the Mössbauer atom in a solid, produces this splitting.

• Magnetic hyperfine splitting

The magnetic dipole interaction causes a Zeeman splitting of the Mössbauer line (magnetic hyperfine splitting): under a magnetic field, it splits the nuclear levels into equidistant non degenerate substrates, and the energy separation between the nuclear levels (DE) is directly proportional to this magnetic field.

The dependence of these parameters upon temperature or pressure can be studied, in addition to the effect of the application of external magnetic fields (in case of magnetic dipole interaction). This technique can be used for the identification of phases, the study of the electronic properties, such as the oxidation state and coordination structures and particle size determination. Unfortunately, not so many elements can be studied by this technique due to the absence of stable isotopes with the right transition energy. The most used isotopes are ⁵⁷Fe, ⁹⁹Ru, ¹²¹Sb, ¹⁹⁷Au and ¹¹⁹Sn. This last one has a transition with an energy of 23.9 keV which is used to study the chemical state and the occurrence of Sn, analyzing the values of the isomer shift and quadrupole splitting [29].

Mössbauer spectroscopy measurements were performed using a $Ca^{119m}SnO_3$ source of 10 mCi nominal activity ($\tau = 293.1$ days). The velocity scale was calibrated by means of a room temperature spectrum of α -Fe recorded with a ${}^{57}Co(Rh)$ source. The hyperfine parameters δ (isomer shift, IS)

and (quadrupole splitting, QS) were determined by fitting the Lorentzian lines to the experimental data. Experiments were performed inside a lead coated chamber, using a scintillation detector to register the spectrum, and then the signal was amplified and conditioned. Samples were exposed to γ -rays till a clear spectra is obtained, using a channel step of dv = 0.05613 mm·s⁻¹. Each spectrum was referenced to the BaSnO₃ signal. Spectra were analyzed using the software Winiso 1.0, with a fitting error of $2\Delta IS = \Delta QS$.

> Raman spectroscopy

This spectroscopic technique is used to observe vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.

In this study the Raman spectroscopy has been utilised to analyse the quality of the carbon coke formed during reaction on the surface of the catalysts, observing the relative intensity of the bands related to graphitic carbon. The instrument used for the analyses is a LabRAM Aramis HORIBA.

> Thermo-gravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a species is heated. The measurement is normally carried out in air or in an inert atmosphere. The behaviour of the sample at determined atmospheres and temperature conditions translate in a loss or a gain of mass, which is registered by the instrument. TGA has been coupled together with another technique in order to obtain complementary information about the thermal behaviour of the sample. The complementary technique used is the differential thermal analysis (DTA) in this technique, temperature changes happening on the sample are compared to the temperature of a reference that is inside the same furnace. The temperature differences between sample and reference are measured in function of the time or the furnace temperature, allowing distinguishing endothermic and exothermic events, like phase changes, combustion or oxidation processes.

Thermo-gravimetric analyses on deactivated catalysts were performed using a *Netzsch* STA409TP TG/DTA system, working in dynamic-air flux mode. Before the analysis, samples were out-gassed overnight to eliminate any residue of volatile products in the samples. The thermal programme (1 hour standby at 60 °C then up to 800 °C), was performed under a flow of synthetic air of 50 ml·min⁻¹, with a ramp of 5 °C·min⁻¹.

> Elemental analysis

CNHS Elemental analysis on spent catalysts was performed with a *ThermoFinnigan Flash EA1112* automatic analyser. This equipment works by high temperature flash combustion in continuous flow, which allows quantifying with precision the amount of carbon, hydrogen, nitrogen and sulfur present in the samples by MS spectrometry analysis.

> Curves deconvolution

The identification of baselines and the deconvolution of data (Raman, DTA) were made with the analytic software Fityk (v. 0.9.8) using a Gaussian as model function for the peaks curve and the Levenberg-Marquardt method of fitting calculations.

2.3 Catalytic testing

The choices made for the practical procedures and the experimental conditions used for the catalytic tests are reported in this chapter. The first part (Chapter 2.3.1) describes how the catalytic test rig has been built-up and the reasons that led to determined choices. In Chapter 2.3.2 are listed the conditions used for the in-situ catalyst treatments and activation before reaction and the reaction operational parameters. In Chapter 2.3.3 are reported the evaluation of hydrogen productivity, the determination of the percentage of reagents conversion and the estimation of the electrical power that is possible to produce with PEM fuel-cells.

2.3.1 Catalytic testing unit

> Test rig build-up

The build-up of the laboratory-scale testing unit for the catalytic dehydrogenation of hydrocarbons calls upon a series of important preliminary considerations: the type of catalyst that will be used (homogeneous or heterogeneous), the kind of reactor (usually a fixed-bed) and the physical phase in which the reaction take place (gas or liquid). From preliminary studies performed in the starting phase of the "GreenAir" project at EADS by Liew et al [7] and from observation on the literature on the dehydrogenation of hydrocarbons (Chapters 1.3.2.2 and 1.4.3) it appears that this process is much more efficient and functional when performed in vapour phase. The reaction of catalytic partial dehydrogenation showed in fact a really low hydrogen productivity when performed in liquid phase [7,30]. The choice for the construction of the testing unit has been then a fixed-bed reactor to perform a gas-phase reaction using a heterogeneous catalyst charge. The hydrocarbons that have been used in this work are in the liquid state in standard conditions

so it is required an evaporator with a sufficient heat exchange to complete evaporate the liquid flow of hydrocarbons entering the system, positioned in front of the reactor part. The following formulas can be used to obtain an estimation of the maximum liquid flow-rate that the evaporator can withstand, reaching the complete evaporation of the liquid phase:

> Fourier's law

$$Q = kA \frac{dT}{s}$$

Q = heat flow (W)

k = thermal conductivity of the material (W·K⁻¹·m⁻¹)

A = heat transfer area (m^2)

dT = temperature difference across the material (K)

s = material thickness (m)

> Heat of evaporation

$$Q_m = \lambda_m + \int_{T_1}^{T_2} Cp \ dT$$

 Q_m = molar heat of evaporation (J) λ_m = latent heat of vaporisation (J·mol⁻¹) C_p = molar specific heat capacity (J·K⁻¹·mol⁻¹) T = temperature (K) The evaporator is over-dimensioned with respect to the operative flow rates, to ensuring a capacity of evaporation up to 3.33 ml/min per centimetre. Therefore in the first region of the evaporator the liquid is already completely evaporated avoiding a distillation effect. The inner diameter is 1 cm, the length 35 cm and the inside is filled with stainless steel leftover curls to optimize the heat exchange. A scheme is showed in Fig. 2:



Figure 2 - Evaporator scheme

The catalytic test unit has been built-up according to the schematic set-up described in Fig. 3:



Figure 3 - Catalytic test rig

The gases entrance (upper left part) include a H_2 , air and Ar line that are controlled by three Brooks mass flow regulators (Delta Smart II Mass Flow SLA5850 series) that are used for in-situ catalyst treatment operations (oxidation, reduction) and for pressurization operations. For security reasons the system provides a valve that prevent the contemporary feed of H_2 and air.

The liquid entrance (lower left part) is composed by a reservoir and a pump for the liquid (UFLC Shimadsu LC-20AD) that allows a liquid flow in the range of 0.05-5 ml \cdot min⁻¹.

Liquid and gas mix before the entrance of the evaporator (central upper part) and enter in the reactor passing through a pre-heating zone that keeps an intermediate temperature between evaporator and reactor avoiding the condensation of the liquid on cold spots.

The reaction part (central part) consists in a stainless steel (type of steel) tubular reactor hold inside a tubular vertical oven with a work temperature range of 20-700 °C. At the rear of the reactor is placed the pressure indicator that is used to regulate the pressure for the reaction (Keller piezoelectric P transmitter).

The gas-liquid separator (central lower part) consists in a stainless steel 1L tank at ambient temperature that allows to fully condensate the dehydrogenated vapour and let the produced hydrogen gas to flow out from a side tubing. Just after the first condenser another stainless steel 0.25 L condenser and a gasket filter are placed to ensure that none of the vapour can reach the P valve and the mass-flow. The pressure valve has a range of 0.1-1.2 MPa. The mass-flow used for measuring the gas outflow (Brooks Delta Smart II Mass Flow SLA5860 series) can be calibrated for different gas compositions adjusting the response factor. The amount of hydrogen produced can be also verified with a bubble flow-meter in parallel to the digital one.

The hydrogen purity is measured with a gas-chromatograph (GC) Agilent 7890A equipped with a thermo-conductivity detector (TCD) for the hydrogen and light hydrocarbon detection and a flame ionization detector (FID) for the traces of heavier hydrocarbon detection. In Fig. 4 a picture of the system is shown:



Figure 4 - Picture of the catalytic testing unit

> Catalytic testing conditions

The general conditions applied for each stage of the process are described in this chapter. Specific reaction conditions may vary from test to test and will be discussed in Chapter 2.4 together with the results. The thermal treatment and catalyst activation are procedures that have been used for all the materials tested in this thesis work and will be explained in detail only once in this chapter.

Before reaction each catalyst was pre-treated in an air flow to achieve complete oxidation of the material before the activation (Table 4).

Parameter	Value
Р	ambient
Т (°С)	500
Air Flow (ml∙min ⁻¹)	55
Time (min)	60

Table 4 - Catal	yst pre-trea	atment co	nditions

Then the catalysts activation was performed by reduction of the metallic active phase (Table 5).

Parameter	Value
Р	ambient
T (°C)	350
H₂ Flow (ml⋅min ⁻¹)	22
Ar Flow (ml⋅min⁻¹)	33
Time (min)	120

The operational parameters for the reactions are presented in Table 6:

Parameter	Value
P (MPa)	0.1-1
т (°С)	350-500
H ₂ recycle (% vol.)	0-7
τ (s)	1-2

Table 6 - Reaction conditions

The catalytic tests were performed on catalyst charges of 1.8 cm³ (around 1 g of catalyst), shaped in form of pellets (0.85-1 mm diameter) without dilution. The contact time (τ) is the time needed for the vapour to pass through the catalytic bed and is calculated at standard temperature and pressure (STP). For the calculation it is assumed that the vapour flowing through reactor is at ambient temperature and pressure; it is important to keep in mind that the real conditions inside the system are different. The catalytic tests are not performed at isotherm conditions: the heat provided by the oven is regulated before reaction in order to reach the temperature set-point and then kept constant. When the reaction starts, the temperature change due to the endothermic effect of the dehydrogenation reaction.

2.3.2 Calculations for the estimation of hydrogen productivity, percentage of conversion and generated electric power

> Hydrogen productivity calculations

$$Prod \ H_2\left(\frac{NL}{h * kg_{cat}}\right) = \frac{((\theta H_{2 out} - \theta H_{2 in})(\frac{ml}{min})}{cat \ weight \ (kg)} * 0.06 * \frac{273.15 \ (K)}{273.15 + T_{ambient}(K)}$$

The total amount of hydrogen produced was calculated by interpolation of the hydrogen productivity curve with a polynomial function and subsequent integration of the function to obtain the hydrogen quantity:

Total Prod
$$H_2(NL) = Cat Weight(kg) * \int_n^m P(x)$$

n, m = integration range (time) P(X) = polynomial function of interpolation

The volumetric % of hydrogen purity is calculated as follow:

$$%H_{2 out} = GC peak area * f$$

f = GC hydrogen response factor

> Hydrogen productivity from representative components of kerosene

For the calculations of hydrogen production from single representative compound of kerosene (or diesel, gasoline), the stoichiometric coefficient for the dehydrogenation reaction has been used. As example, the reaction of methylcyclohexane dehydrogenation is reported in Fig. 4:



Figure 5 - Methylcyclohexane dehydrogenation reaction

The calculation for the percentage of hydrogen for each reagent is then made with the following formulas:

 $Volume of fed liquid (ml) = \theta_{pump} \left(\frac{ml}{min}\right) * t_{reaction}(min)$ $V_i(ml) = \% vol_i * Volume of fed liquid (ml)$ $V_i converted (ml) = V_i(ml) * \chi$ $mol_i converted = V_i converted (ml) * \frac{\delta_i(\frac{g}{ml})}{PM_i(\frac{g}{mol})}$ $Prod H_2 for the reagent i (\%) = \frac{mol_i converted * C}{mol_{total H2 produced}} * 100$

C = stoichiometric coefficient of the hydrogen in the reaction for the reagent i χ = conversion θ = liquid flow (ml·min⁻¹)

> Calculation of the % conversion

The conversion of the liquid hydrocarbons has been calculated as follows:

$$\chi = \frac{\% vol_{in} - \% vol_{out}}{\% vol_{in}}$$

$$\% vol_{out} = f * GC peak area$$

f = GC response factor for the considered reagent

> Electrical power estimation

The estimation of the quantity of electric energy generated by a fuel-cell stack fed with the produced hydrogen is here described. Assuming that the FC work at a potential of 0.7 V the current necessary to produce 1 kW of energy is calculated as follows:

$$I(A) = \frac{P(W)}{V(V)} = \frac{1000(W)}{0.7(V)} = 1,4286 \ (kA)$$
$$1A = \frac{1C}{1s}$$

Considering that each mole of H_2 produce 2 mol of e⁻ the number of hydrogen liters to achieve that value of current it will then be:

$$\frac{2 * H_2(mol) * N_a}{K_e} = \frac{192981,9 (C/mol)}{1000 * 3600} = 0,053606 \left(\frac{kA * h}{mol}\right)$$

Na = Avogadro's constant Ke = Coulomb's constant

$$H_2\left(\frac{l}{h}\right) = \frac{1,4286\ (kA)}{0,053606\ (\frac{kA*h}{mol})} = 26,65\ \left(\frac{mol}{h}\right)*22,4\ \left(\frac{l}{mol}\right) = 596,96\ (\frac{l}{h})$$

Considering converting all the hydrogen in more than one passage through the stack and an efficiency of FC of 50% the amount of hydrogen that need to be feed is:

$$H_2 feed\left(\frac{Nl}{h}\right) = 596,96 \, \left(\frac{l}{h}\right) * \frac{273,15}{293.15} * \frac{50}{100} = 1112,5 \, \left(\frac{Nl}{h}\right) \sim 1000 \left(\frac{Nl}{h}\right)$$
2.4 The partial dehydrogenation of kerosene: experimental results

The sections below describes the process of catalyst screening and catalyst development towards the goal of achieving a hydrogen production of at least 1000 NL·h⁻¹·kg_{cat}⁻¹ with a purity > 95 % vol. for a duration of 100 hours.

2.4.1 Baseline materials: characterisation and catalytic results

> Surface and structural properties

To investigate the feasibility of the hydrogen generation via PDh of kerosene and reach the best performances, the work started with baseline materials including the reference alumina supported catalyst JM1. As described in Chapter 2.1.1, the first reference material is a 1 % Pt-1 % Sn/ γ -Al₂O₃ and JM2 is a 1 % Pt-1 % Sn supported on a BaO modified γ -Al₂O₃. The other two baseline materials studied in this work are commercial reforming catalysts purchased from UOP and have been tested with the purpose of evaluating the activity of some existing reforming catalyst compared to the materials developed in this project for the PDh of kerosene.

The baseline materials have been analysed via XRD diffraction technique in order to obtain information on the crystalline structure of supports (Fig. 6).



Figure 6 - XRD profiles for the baseline materials (dotted lines: Al₂O₃ phase)

The XRD analyses confirm that all the materials are γ -alumina with low cristallinity supported catalyst. The aluminium oxide pattern (ISCD#00-046-1131) can clearly match the signals while peaks related to Pt, Sn or SnO₂ are not detected. The fact that Pt and Sn are not identified could be explained by the low metal concentration and their high dispersion; the weak contributions related to the Pt metal are overlapped by the broad aluminium oxide diffraction. The differences noticed between the four different materials in the zone 30-35 20 angle don't match any metallic phase and can be attributed to the different degree of cristallinity of the alumina supports.

The porosity of the materials has been studied and the results for the four reference materials are shown in Fig. 7:



Figure 7 - Surface and porosity analysis performed on the baseline materials

All the materials show isotherms of adsorption and desorption with the characteristic hysteresis loop of the type IV in the IUPAC classification, typical for mesoporous adsorbents, but they have differences in pore size and volume. The two Johnson Matthey materials JM1 and JM2 display lower values of specific surface area with 133 m²·g⁻¹ for the first and 96 m²·g⁻¹ for the second. The difference between the two materials is the pore size distribution, JM1 has a higher surface area with smaller pores around 9-10 nm

while JM2 has a lower surface area with larger pores. The pore size distribution for JM2 is very broad with a prevalence around 35-45 nm but also showing the presence of smaller pores.

The two UOP catalysts have higher surface area with values of 175 m²·g⁻¹ and 196 m²·g⁻¹ for UOP1 and UOP2 respectively. The first one presents a broad pore size distribution centred at 22 nm while the second has a very narrow distribution centred at 20 nm. Overall even though the four catalysts are all supported on γ -Al₂O₃, they present very different surface and porosity characteristics.

The acidity properties of the reference materials have been analysed by thermal programmed desorption of ammonia, the profiles obtained are shown in Fig. 8:



Figure 8 - Ammonia desorption curves for the baseline materials

The overall acidity value is the highest for the UOP2 catalyst followed by UOP1, JM1 and at last JM2 that has the lowest acidity value. The distribution of the acid sites has a similar shape for the catalysts UOP1, UOP2 and JM1 with a distribution of acid sites in two main peaks which differentiate for the overall signal intensity. The catalyst JM2 displays a significantly lower area of the first peak corresponding to the weak acidity. It seems that the modification of the alumina with BaO carried out by Johnson & Matthey has the effect of decreasing the overall acidity in particular decreasing the weak acid sites concentration [31].

> Activity in the partial dehydrogenation reaction

Catalytic tests have been performed for the duration of 4 hours with the baseline materials, using as reagent a low sulfur kerosene Jet A-1 provided by Total (LSK S \leq 3 ppm). The operational conditions are 450 °C, 1 MPa, τ = 2s, 7% vol. H₂ recycle. The evolution hydrogen productivity with time is shown in Fig. 9:



Figure 9 - Evolution of hydrogen productivity with time for the baseline materials

The catalyst JM1 undergoes complete deactivation after 11.1 h that is far from the minimum required by the targeted application. The hydrogen productivity is low scarce although the hydrogen purity is high enough to allow the gas to be fed directly to a fuel-cell system.

The JM2 material, shows much better performances with an extrapolated lifetime (corresponding to the complete deactivation) of 32.5 h, an average H_2 production during the 6 hours reaction of 2500 NL·h⁻¹·kg_{cat}⁻¹ and a purity of 97.2 % vol.

The two commercial reforming catalysts supplied by UOP show intermediate performances compared to the two JM catalysts with lifetimes of 18.6 hours and 18.3 hours for UOP1 and UOP2 respectively. UOP2 has the higher hydrogen productivity, but it also displays the lowest hydrogen purity of 96.7 % vol. The initial hydrogen productivity seems to be higher for the two UOP catalysts but the deactivation in the first hour of reaction is very fast. This trend could be related to the acid sites distribution in the UOP materials. They display a higher concentration of stronger acid sites respect the JM materials, probably leading to a higher conversion of the kerosene through secondary reactions like hydrogenolysis and cracking. This secondary reactions give a little contribution in terms of hydrogen produced, but accelerate significantly the deactivation via carbon coke deposition [32,33].

The JM's materials display similar overall value of acidity but the distribution of weak-mild acid sites is different. The modification of the alumina with BaO has the effect of decreasing the weak acid sites concentration; however this is not sufficient to explain the performance difference. The alumina modified with BaO in JM2 not only has a different acidity but also a larger pore size distribution which can contribute to the better performance of this material. From the result obtained it is possible to conclude that commercial reforming catalysts and dehydrogenation catalysts can be used for the partial dehydrogenation of kerosene, but to achieve results that will allow the application of such a system for electricity production on-

board an airplane it will be fundamental to develop more efficient catalysts optimised specifically for this application.

As JM2 catalyst appeared to be the best baseline material, a 24 hour catalytic test has been performed in order to have a more accurate evaluation of the performance and lifetime. The reaction conditions are the same used for the previous test. The hydrogen productivity plot is showed in Fig. 10:



Figure 10 - Hydrogen productivity curve for JM2 long term testing on LSK

The reproducibility of the catalytic test is very good: the 6 hours test results, previously discussed (black dots), and those of the 24 hours test (orange line) are perfectly overlapped, which attests a good reproducibility of the experiments. The extrapolation on the long term test lead to an estimation of the lifetime of 70.1 hours, which is an encouraging value for the target application. However the hydrogen purity at 24 hours is slightly lower than at 6 hours, but the main impurity is CH_4 therefore it should not affect noticeably the efficiency of a PEM-FC stack.

2.4.2 Optimisation of the operating conditions for the partial dehydrogenation of kerosene

The reaction operating conditions also affect the performance in terms of hydrogen production and catalyst stability. The temperature must be high enough to guarantee an acceptable reaction kinetic but low enough to avoid cracking. The partial pressure and the amount of hydrogen in the feed introduced to simulate the recycling are also very important factors because they shift the equilibrium of the reaction. The last parameter to take in consideration is the contact time, which influences the degree of conversion of the reagents and the selectivity towards determined products.

At the beginning of the "GreenAir" project, the catalyst JM1 was utilised as reference material to optimise the operating conditions for the PDh of kerosene, which are 450 °C, 0.1 MPa, $\tau = 2s$ and a 7% vol. hydrogen recycling [6]. The material JM2 shows a strong improvement respect JM1, therefore, in order to achieve an even better performance, a further optimisation of the operating conditions have been performed in the course this work. The objective is the fine tuning of the operating conditions in order to minimise the effect of the catalyst deactivation via carbon deposition. The reagent used was LSK, the pressure during the catalytic testing was 1 MPa (the minimum pressure needed for an eventual purification by pressure swing absorption PSA). Contact time and temperature have been varied in order to screen the best conditions. In order to screen the conditions two temperature values (400 °C and 450 °C) and two contact time values (1s and 2s) have been selected for conducting the initial tests. The hydrogen productivities registered during these tests are shown in Fig. 10. A summary of the catalytic performance and the analyses on carbon deposition are reported in Table 8.



Figure 11 Hydrogen productivity plots for JM2 operating conditions screening

Table 7 - Coke and performance summary for the catalyst JM2

Conditions	Lifetime (h)	Coke %	H ₂ /Kerosene (NL/L)	Coke/H ₂ (mg/mol)	H ₂ purity (% vol.)
450 °C τ = 1s	20,9	3,3	44,0	130,5	96,9
450 °C τ = 2s	32,5	3,0	73,9	132,4	97,2
400 °C τ = 1s	38,7	1,8	21,9	133,7	97,7
400 °C τ = 2s	12,3	2,6	30,1	269,5	96,5

At 400 °C, $\tau = 2$ s the lifetime registered is the shortest, a low amount of hydrogen is produced per litre of kerosene and the ratio of carbon coke per mole of hydrogen produced is the highest. The highest hydrogen productivity is displayed at 450 °C, $\tau = 1$ s but the deactivation is very fast and the lifetime is limited (20.9 h). The higher lifetime is obtained for T = 400 °C, $\tau = 1$ s, but it is important to observe that the amount of hydrogen produced per litre of kerosene is the lowest. This is a very important factor to consider because the total efficiency of the system depends also on the energy necessary to evaporate the kerosene before the reaction. As a consequence it has been chosen to adopt the conditions 450 °C, $\tau = 2s$ even if the lifetime is slightly lower than the lifetime at 400 °C, $\tau = 1s$, because the productivity in terms of litres of hydrogen produced per litre of kerosene is higher (73.9 NL·L⁻¹ against 21.9 NL·L⁻¹).

In terms of hydrogen purity (after 4 hours of reaction), no drastic changes are noticed varying the operating conditions, with values in the range of 96.5 - 97.7 % vol. The hydrogen purity seems to be inversely proportional to the catalyst activity: the test at 450 °C, $\tau = 1$ s, that show the highest H₂ production, has a purity value of 96,9 % vol., while for the tests at 450 °C, $\tau = 2$ s and 400 °C, $\tau = 1$ s, which have lower H₂ productivities, the purity is higher (97.2 % and 97.7 % vol. respectively). There is an exception for the test at and 400 °C, $\tau = 2$ s which surprisingly presents the lower productivity, the lower hydrogen purity and the lowest catalyst lifetime. This effect could be caused by mass transfer problems that occur in these particular operative conditions.

In order to obtain more detailed information on the deposited carbon coke formed, the spent catalysts have been analysed by Raman spectroscopy. It is possible to identify the peaks related to ordered carbon D1 (1350 nm) and G (1590 nm) that are clearly visible, while the others are related to disordered carbon [34,35]. In Fig. 12 are reported the Raman spectra in the region characteristic of carbon vibration, obtained for the spent catalysts collected after catalytic reaction at two different contact time (1s-2s) and two temperature (400 °C-450 °C).



Figure 12 - Raman spectra obtained from the spent catalysts after reactions at different conditions

For both temperatures, when the contact time increases from 1 s to 2 s, the contribution of the D1 and G peaks increase. With a longer contact time the dehydrogenation ratio is higher and leads to a more ordered carbon deposit, which contain a low amount of hydrogen (more graphitic). The same effect is noticed when for a given contact time the temperature is increased from 400 °C to 450 °C, resulting in a higher dehydrogenation ratio and a preferential formation of graphitic carbon [34,35].

The compromise between lifetime and productivity observed at this operating conditions have been obtained for T = 450 °C, τ = 2s and T = 450 °C, τ = 1s (lifetime > 30 h, deactivation factor < 100 NL·h⁻¹, initial productivity > 1500 NL·h⁻¹·kg_{cat}⁻¹) so, in order to investigate more precisely the effect of temperature and contact time, a test at intermediate conditions (T = 425 °C, τ = 1,5 s) have been performed. The results of hydrogen productivity are shown in Fig. 13.



Figure 13 - Hydrogen productivity curves for JM2 at intermediate conditions

As expected, the hydrogen productivity and stability for 425 °C, $\tau = 1,5s$ lies in between those obtained at 450 °C, $\tau = 2s$ and 400 °C, $\tau = 1$ consequently after this screening the values 450 °C, $\tau = 2s$ have been chosen as the best conditions for the partial dehydrogenation of LSK with the JM2 catalyst.

2.4.3 Catalysts supports screening

The results obtained with the baseline materials (Chapter 2.4.1) indicate that the γ -Al₂O₃ is a good candidate as support for the PDh reaction catalyst, but it also emerged that differences in the support properties can have a significant influence on the catalyst performance. Different catalyst supports, with different texture and surface properties have been characterised in order to investigate the effect of the support on the properties of Pt-Sn catalysts. The materials used as support were two zeolites (USY and YNa), two montmorillonites (K-10 and K-30 named MM1 and MM2 respectively), two mesoporous templated silicas (SBA1 modified with CeO and SBA2 modified with ZrO and CeO) and an oxide derived from a hydrotalcite (HT MgO/Al_2O_3). The performances and properties are compared to the catalysts JM1 and JM2 presented Chapter 2.4.1. The catalysts have been prepared as explained in Chapter 2.1.2 with 1 % Pt-1 % Sn as active phase.

The porosity of the materials have been analysed via adsorption/desorption of nitrogen and the acidity have been measured by NH_3 -TPD. The results are summarised in Table 9:

	Surface Area	Pore Volume	Pore Size	Acidity
	(m ² ⋅g ⁻¹)	(cm ³ ·g ⁻¹)	(nm)	(µmol _{ℕH3} ·g⁻¹)
USY	531	0.323	2.5	406
YNa	596	0.342	2.3	337
JM1	133	0.421	12.7	96
JM2	96	0.950	39.5	126
MM1	215	0.359	6.6	69
MM2	196	0.342	6.3	57
SBA1	417	0.877	8.2	125
SBA2	392	0.849	7.9	136
HT	126	0.323	9.9	111

Table 8 - Surface properties of the materials for supports screening work

The materials are all mesoporous or super-microporous and cover a wide range of surface areas and pore size distributions. The surface area goes from the highest values of 500-600 m²·g⁻¹ for the zeolites to the lowest value of 126 m²·g⁻¹ for the basic oxides. The pore size distribution is monomodal for all the materials and goes from the small value of 2.3 nm (close to micropores region) for the zeolite YNa to the 39.5 nm for the alumina of the catalyst JM2. This selection of materials presents very different surface properties.



The acidity distribution of the materials have been measured by thermal desorption of ammonia. The results are shown in Fig. 14.

Figure 14 - NH₃-TPD profiles for the series of Pt-Sn supported catalysts

The NH₃-TPD results are reported in two separate graphs with different scales: the zeolites that present high acidity level, with JM1 as reference in the bottom graph and the other materials (SBA, MM, HT, JM2) with lower acidity level in the top graph. The total acidity of the catalysts can be described as

follow: zeolites >> SBA > aluminas, HT > montmorillonites. The zeolites YNa and USY have an overall acidity that is more than threefold the acidity of the others materials. The SBA materials show a distribution of the acid sites different from the others, with a higher concentration of mid and low strength acid sites. The effect of the acidity on the performance will be discussed in parallel to the catalytic results.

The catalytic tests have been carried out at 450 °C, 1 MPa, and $\tau = 2$ s with LSK as feedstock. The hydrogen productivities registered during the experiments are reported in Fig. 15.



Figure 15 - Hydrogen productivity plots and performances table for the support screening series

The lowest productivity is observed with the montmorillonite and zeolite supported catalysts which all have a similar behaviour, below the European project target of 1000 NL \cdot h⁻¹ \cdot kg_{cat}⁻¹ after the first hour of reaction. The hydrogen purity for the MM and zeolite materials is in the range of 96.3-96.7 % vol.

The highest hydrogen productivity is obtained with the SBA2 material which shows the best initial activity (initial is considered at 60 min when the steady state is reached), but followed by a rapid and constant deactivation. This catalyst has the lowest extrapolated lifetime and the lower hydrogen purity value (94.4 % vol.). SBA1 seems to be more stable after the first hour of reaction and has both higher lifetime and hydrogen purity. The catalyst HT presents the lowest lifetime together with SBA2 (around 10 hours) and a low hydrogen purity value (95.2 % vol.). The best compromise between hydrogen production, purity and stability seems to be the alumina supported catalyst JM2 with a lifetime of 34.8 hours and a H₂ purity value of 98.2 % vol.

The activity of zeolites and montmorillonites are similar but the deactivation of zeolites seems more rapid, this is probably due to their high level of acidity (> 300 μ mol_{NH3}·g⁻¹) that can favour secondary reactions leading to coke formation. Another cause could be the small pore volume ($\approx 0,35 \text{ cm}^3 \cdot \text{g}^{-1}$) combined to a small diameter pores ($\approx 2,3 \text{ nm}$), which can be easily clogged by the deposit of the coke formed [3]. Montmorillonites have the lowest acidity (60-70 μ mol_{NH3}·g⁻¹) which, together with the low pore volume value (0.35 cm³·g⁻¹), could explain the low hydrogen productivity. The mixed oxides catalyst has an intermediate acidity (111 μ mol_{NH3}·g⁻¹) which lead to an average initial activity, but the deactivation is really fast (lifetime 10.5 h) due to low surface area (126 m²·g⁻¹) and pore volume (0.32 cm³·g⁻¹). The two materials with sufficiently high productivity with time, to fulfil partially the objective of the "GreenAir" project, are JM2 and SBA2. The first has a lower initial activity but display a better stability while the second has an opposite behaviour.

This study suggests that higher acidity is related to higher initial hydrogen productivity, but also causes a rapid deactivation [33,36]. On the other hand for the porosity properties, higher surface area and pore volume are associated to better stability.

Other important factors, which have not been considered in this support screening, are the metals-support interaction and the metal dispersion. From the information gathered it seems that an acidity in the range of 100-200 μ mol_{NH3}·g⁻¹ with prevalence of weak-mild acid sites and a high pore volume are beneficial for the partial dehydrogenation of kerosene.

2.4.4 Catalyst active phase optimisation

Materials optimisation can be achieved either by modification of the catalyst support or by modification of the catalyst itself. The catalyst that has been mainly used in this thesis work is a combination of Pt and Sn. Platinum is the most active metal for hydrocarbons dehydrogenation reaction while tin is used to modulate the platinum activity and increase the stability. It is demonstrated that the addition of a third metal to Pt-Sn/Al₂O₃ can lead to improvement of the catalytic properties, and examples of enhanced trimetallic catalysts for reforming or dehydrogenation can be easily found (Pt-Sn-M/Al₂O₃ M = Re, Ir, Ge) [18,20,37]. One example, reported by Bocanegra et al. [23] that carried out a study on Pt-Sn-In/MgAl₂O₃ catalysts for n-butane dehydrogenation, shows that indium addition remarkably enhances the catalyst stability and inhibits undesired hydrogenolysis reactions.

In this part of the work, the effect of addition of In to $Pt-Sn/\gamma-Al_2O_3$ catalysts has been investigated. This study is presented in the following article published in the scientific journal "Applied catalysis B: Environmental":

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Study of the effect of addition of In to $Pt-Sn/\gamma-Al_2O_3$ catalysts for high purity hydrogen production via partial dehydrogenation of kerosene jet A-1



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ABSTRACT

The partial dehydrogenation (PDh) of hydrocarbons is emerging as a promising technology for high purity H₂ production, suitable to directly feed a fuel cell stack. In particular for direct on-board application this method has the advantage of avoiding the problem of gaseous or liquid hydrogen storage and allows the recovery of the dehydrogenated hydrocarbons for valuable usage. Partial dehydrogenation of hydrocarbon blends like kerosene could be a convenient way to increase the energy efficiency in aviation on-board applications. A series of trimetallic catalysts (1%Pt-1%Sn-[x]%ln/ γ -Al₂O₃ with *x* = 0.25, 0.5, 0.75, 1) has been prepared for low sulfur kerosene dehydrogenation. Particularly remarkable is the enhancement of activity and stability observed for ln/Pt/Sn weight ratio of 0.5:1:1 which provides an average H₂ production of 2900 NL h⁻¹ kg_{cat}⁻¹ (86.7 NL L_{kerosene}⁻¹), sufficient to produce ≈2.9 kW of electricity. The hydrogen yield achieved is 6.4% w/w with a TOF (turnover factor) of 0.69 s⁻¹.

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1. Introduction

Increasing the efficiency in transportation technologies is essential for a sustainable development. The search for alternative power sources with low pollutant emissions and affordable cost is driving a great research effort in the last decade [1,2]. In this context, fuel cells are a very attractive technology due to their high efficiency, making them a strong candidate for the integration into the energy system. A key problem for their employment, especially for transportation and on-board applications, is the storage of the hydrogen fuel [3]. Currently physical storage devices like cryogenic liquid H₂ tanks or highly compressed gaseous H₂ tanks are the closest to the DOE (U.S. Department of Energy) and European specifications but they have some drawbacks: compressed H₂ needs a large volume tank (depending on the pressure in the tank) and the higher the tank pressure, the thicker has to be the tank. Liquid H₂ has a lot of evaporation losses and needs a high amount of energy for the liquefaction [4,5]. Other technologies such as chemical storage using hydrogen absorbing alloys or organic hydrides are gaining increasing interest

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http://dx.doi.org/10.1016/j.apcatb.2014.06.003 0926-3373/© 2014 Elsevier B.V. All rights reserved. as they can avoid the problems associated with liquid and high pressure storage. Chemical storage via hydrogenation/dehydrogenation of liquid hydrocarbons is increasingly considered a viable method and, in addition, the absence of oxygen in the process of hydrocarbons dehydrogenation makes it suitable for producing a hydrogen stream free of CO, which can be used directly to feed a fuel cell stack, potentially without further purification or treatment [6–8].

Partial dehydrogenation of hydrocarbon blends like kerosene could be a convenient way to achieve lower emissions in aviation applications and contribute to higher energy efficiency. On-board electricity generation is supplied by the auxiliary power unit (APU) (90 kW based on Airbus A320 data) and is currently generated with a turbine [9]. The implementation of a dehydrogenation reactor coupled with a fuel cell system for electricity generation instead of the turbine would lead to many advantages: typical turbine efficiency for kerosene to electricity conversion is only 15% and can be enhanced; partially dehydrogenated kerosene can be recycled to the engines; fuel cell emissions are not contaminant which would reduce air traffic pollution [10].

A significant number of supported-metal catalysts have been developed for hydrocarbon dehydrogenation, and the most widely used are based on supported Ni or Pt often in combination with other metals. The properties of the support also have a great importance: acidity, pore size and pore volume are crucial factors that strongly affect the catalyst performance [8,11-20]. For gas-phase kerosene partial dehydrogenation in particular, there are already a few examples of the use of the catalytic system based on Pt-Sn/Al₂O₃ showing encouraging results with kerosene surrogates. Nevertheless, the deactivation rate of the catalyst is still very high when the reagent used is a real commercial kerosene jet A-1 with lifetimes in the range of few hours [21–25]. Lucarelli et. al. [23] show how the majority of the hydrogen produced comes from the conversion of cyclo-alkanes leaving the linear paraffins, which are the primary component of kerosene (around 65% vol.), almost unconverted. Those preliminary studies indicate that the overall conversion of hydrocarbons is sufficiently low to allow the reutilisation of the dehydrogenated product as fuel. As reported in previous studies, the optimal Pt-Sn ratio for this reaction giving a good compromise between hydrogen productivity and catalyst stability is around 1:1 w/w. The acidity of the catalyst is an important factor, as high content of strong acid sites shifts the selectivity towards undesired cracking reaction and formation of coke [26,27]. The importance of kerosene sulfur content is also a key parameter to consider, as this element is a poison for many catalyst active phases [26]; for this reason in the present study a low sulfur content commercial jetA-1 kerosene (ULSK) has been used in order to focus on the deactivation by carbon coke deposition.

The catalyst system based on Pt-Sn supported on γ -Al₂O₃ is well-known and widely used in various processes of reforming and dehydrogenation: amongst these, naphtha reforming is one of the more frequent [28,29] together with paraffin to olefin dehydrogenations [27,30,31]. It is demonstrated that the addition of a third metal to Pt-Sn/Al₂O₃ can lead to improvement of the catalytic properties, and examples of enhanced trimetallic catalysts for reforming or dehydrogenation can be easily found (Pt-Sn-M/Al₂O₃ M = Re, Ir, Ge)[32–34]. However, the literature concerning the effect and interaction of In with the Pt-Sn for dehydrogenation reaction is very limited. One of the rare examples, reported by Bocanegra et al. [35] that carried out a study on Pt-Sn-In/MgAl₂O₃ catalysts for nbutane dehydrogenation, shows that indium addition remarkably enhances the catalyst stability and inhibits undesired hydrogenolysis reactions.

In this work the effect of addition of In to Pt-Sn/ γ -Al₂O₃ catalysts has been investigated by synthesising a series of catalysts with increasing In loading and evaluating the material properties by several characterisation techniques (X-Ray diffraction, X-Ray fluorescence, NH₃ temperature programmed desorption, H₂ temperature programmed reduction, adsorption–desorption of N₂ and H₂ chemisorption) comparing them to a Pt-Sn catalyst as reference. The catalysts have been tested on a laboratory scale plant for the reaction of partial dehydrogenation of low sulfur jetA-1 reaction, analysing the role of In on Pt dehydrogenation activity and on catalyst lifetime. The mechanisms of catalyst deactivation have also been studied by analysis on the carbon coke produced during the reaction using Raman spectroscopy, elemental analysis and thermo-gravimetric analysis.

2. Materials and methods

2.1. Catalyst preparation

co-impregnation to the previously obtained In/Al_2O_3 using aqueous solutions of $H_2PtCl_6\cdot 6H_2O$ (*Alfa Aesar*) and $SnCl_2\cdot 2H_2O$ (*Acros*), to give a ratio 1% wt. Pt and 1% wt. Sn (mol. ratio Pt/Sn = 0.61). The tin precursor was dissolved in 1 M HCl and then mixed with the platinum salt solution upon which the solution turns red-brown due to the formation of a $[PtCl_2(SnCl_3)_2]^{2-}$ complex. In the literature it is reported that the procedure of Pt-Sn co-impregnation leads to a higher amount of Pt_xSn alloy formation that lead to improved catalyst stability [36,37]. After drying the impregnated materials overnight at 80 °C, they were thermally treated in air at 120 °C for 2 h and then at 560 °C for 2 h (heating ratio 2 °Cmin⁻¹). The catalysts were labelled as "Cat-In[x]" where x is the percentage in weight of indium. A reference Pt-Sn bimetallic catalyst without In was also synthesised with the same procedure and it was labelled as "Cat-Ref".

2.2. Characterisation techniques

Structural investigation of the samples was performed by X-Ray diffraction (XRD), using a *PANalyticalX'Pert* diffractometer, with CuK_{α} as radiation source (λ = 0.15418 nm, 40 kV, 25 mA); the acquisition time was 60 min. Phase identification was performed using *HighScore* software by *PANalytical*.

Chemical composition verification of the samples was performed by X-Ray fluorescence (XRF) using a *PANalytical AXIOS MAX* instrument, with a Rh radiation source (4 kW). Elemental quantification was performed using *SUPER-Q* software.

Adsorption–desorption N₂ isotherms were carried out at -196 °C with an *ASAP2020* system from *Micromeritics*. Samples were out-gassed at 200 °C for 8 h under a vacuum of 66.7 Pa. Specific surface area was calculated using the BET (Brunauer, Emmett and Teller) method and pore size distribution using the BJH (Barrett, Joyner, Halenda) method using the *ASAP2020* implemented software; pore volume values are related to the condensation point at $P/P^0 = 0.99$.

The acidity of the materials was studied by NH₃ temperature programmed desorption (NH₃-TPD), using an *Autochem 2910* automatic system from *Micromeritics*. Samples were heated to 550 °C in a He flow of 30 ml min⁻¹ (heating ratio 5 °C min⁻¹) then cooled to 100 °C. Then a flow of 20 ml min⁻¹ pure NH₃ was passed through the samples for 1 h, which were then flushed with He at 100 °C for 1 h. NH₃ was thermally desorbed up to 600 °C with a heating ramp of 10 °C min⁻¹ and the signal was registered using a TC (thermal-conductivity) detector. The apparatus was calibrated using Ni(NH₃)₆Cl₂ as NH₃ source.

H₂ temperature programmed reduction (H₂-TPR) war performed in an *Autochem 2910* apparatus. The samples were oxidised in synthetic air (30 ml min⁻¹; 500 °C, 5 °C min⁻¹), then after cooling to 50 °C, a 30 ml min⁻¹ flow of H₂(5%)/N₂ mixture was passed over the sample, which was then heated at 10 °C min⁻¹ up to 700 °C, registering the H₂ consumption with a TC detector.

 H_2 chemisorption was performed in an Autochem 2910 apparatus. The samples were heated in air flux (30 ml min⁻¹; 500 °C, 5 °C min⁻¹) and then reduced with a $H_2(5\%)/N_2$ mixture at 350 °C. Desorption of physisorbed hydrogen was carried out in N_2 flow at 380 °C for 1 h. Pure H_2 pulses adsorption was recorded at 40 °C. The stoichiometry assumed for the dispersion calculation was $Pt/H_2 = 2$ and for the particles size calculation the shape considered was a hemisphere.

Thermo-gravimetric analyses on deactivated catalysts were performed using a *Netzsch* STA409TP TG/DTA system, working in dynamic-air flux mode. Before the analysis, samples were outgassed overnight to eliminate any residue of volatile products in the samples. The thermal programme (1 h standby at 60 °C then up to 800 °C), was performed under a flow of synthetic air of 50 ml min⁻¹, with a ramp of 5 °C min⁻¹.



Fig. 1. Laboratory scale bench test scheme.

CNHS Elemental analysis on spent catalysts was performed with a *ThermoFinnigan Flash EA1112* automatic analyser.

The identification of baselines and the deconvolution of data were made with the analytic software *Fityk* (v. 0.9.8) using a Gaussian as model function for the peaks curve and the Levenberg-Marquardt method of fitting calculations.

2.3. Catalytic testing of kerosene PDh reaction

The PDh reaction on low sulfur content kerosene jet A-1 (S<3 ppm), was performed in a stainless steel fixed-bed tubular reactor. Before the reaction, the catalysts were oxidised in synthetic air flow (55 ml min⁻¹) at 500 °C and reduced in a H₂/Ar flow (55 ml min⁻¹-4:6 v/v) at 350 °C and atmospheric pressure for 2 h. The kerosene was brought with a volumetric pump (Shimatzu $LC20AD-0.53 \text{ ml min}^{-1}$) to the evaporator and then kerosene vapour (93% vol.) was mixed with a 7% vol. of H₂ (used to simulate a recycle) before entering the reactor containing pelletised catalyst (d = 1-0.85 mm; $V_{\text{cat.bed}} = 1.8 \text{ cm}^3$; mass average $\approx 1 \text{ g}$) at $T = 450 \circ C$ (previous work shows that this is the optimal T for the reaction [23]) and P=10 bar. These flows were regulated in order to obtain a contact time $\tau = 2 s$ (calculated at standard temperature and pressure). A scheme of the reaction rig is shown in Fig. 1. After condensation of the dehydrogenated kerosene, hydrogen production (NL h⁻¹ kg_{cat}⁻¹) was calculated from measurement of the gas out-flow with a digital mass flow meter (Brooks5860S1 Smart II mass flow meter), and the data processed with LabView 8.2 instrumentation software. Hydrogen production was calculated following the equation (Eq. (1)):

a HP-PLOT/Q column with a Flame Ionisation Detector (FID) to analyse the traces of light hydrocarbons (C4–C5) present in the gas stream. Hydrogen yield is calculated as ratio between hydrogen produced and total amount of hydrogen in the kerosene used for the reaction (w/w). Catalyst lifetime is calculated by linear extrapolation of the H₂ productivity curves between 180 and 360 min of TOS (time on stream). Deactivation % is calculated from the ratio between initial and final H₂ productivity.

3. Results and discussion

3.1. Structural and surface characterisation

In Fig. 2 some of the most significant XRD patterns are reported. All the materials show the typical diffractions lines of γ -Al₂O₃ but there is no appreciable difference between the diffraction pattern of the Al₂O₃ support and those of fresh catalysts. In fact, none of the catalysts exhibit peaks attributable to Pt crystalline phases; this could be due to factors such as the low platinum content and high dispersion of the metals. From observation of the XRD patterns the only noticeable difference is between fresh and spent material, the latter present peaks characteristic of graphite carbon (25 and $42^{\circ}2\theta$).

In Table 1 the composition of the catalysts measured by XRF analysis is summarised, showing a comparable amount of Pt and Sn for all materials. The nominal value is 1% w/w for both Pt and Sn and the results are close to this for Pt (average 1.0% w/w) and

$$H_2 \text{ production rate} = \frac{\text{Produced Gas OutFlow (NL/h) - Hydrogen Flow Recycle simulation (NL/h)}}{m_{\text{cat}} (\text{kg})} (1)$$

Hydrogen purity was analysed with a gas chromatograph *Agilent7890A* equipped with a dual column system. A *HP-PLOTmolesieve 5A column* connected to a Thermal Conductivity Detector (TCD) was used to analyse the composition of the gas-phase produced by the reaction (hydrogen, methane, propane) and

slightly lower for Sn (average 0.6% w/w). The In contents measured are also lower than the nominal amount impregnated, possibility due to the method used for the integration: the values are calculated using calibrations for the reduced metal (oxidation state zero) while (particularly for Sn), the average oxidation state may

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Fresh	materials	characterisation	parameters	
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1.5					
Pt (%) ^a	Sn (%) ^a	In (%) ^a	Metallic dispersion (%) ^b	Metal particles size (nm) ^b	Total acidity $(\mu mol NH_3/g)^c$
-	-	-	-	3 — 3	127.1
0.92	0.63	0.00	48.7	2.3	126.0
0.97	0.61	0.13	43.4	2.6	132.0
1.05	0.65	0.24	49.3	2.3	123.5
0.96	0.63	0.34	41.3	2.7	120.0
1.00	0.57	0.49	35.7	3.2	117.7
	Pt (%) ^a - 0.92 0.97 1.05 0.96 1.00	Pt (%) ^a Sn (%) ^a - - 0.92 0.63 0.97 0.61 1.05 0.65 0.96 0.63 1.00 0.57	Pt (%) ^a Sn (%) ^a In (%) ^a - - - 0.92 0.63 0.00 0.97 0.61 0.13 1.05 0.65 0.24 0.96 0.63 0.34 1.00 0.57 0.49	Pt (%) ^a Sn (%) ^a In (%) ^a Metallic dispersion (%) ^b - - - - 0.92 0.63 0.00 48.7 0.97 0.61 0.13 43.4 1.05 0.65 0.24 49.3 0.96 0.63 0.34 41.3 1.00 0.57 0.49 35.7	Pt (%) ^a Sn (%) ^a In (%) ^a Metallic dispersion (%) ^b Metal particles size (nm) ^b - -

a XRF.

^b H₂-chemisorption.

^c NH₃-TPD.



Fig. 2. XRD patterns of the alumina support and some of the catalysts (--- grey dotted lines: γ -Al₂O₃; \downarrow down arrow: carbon coke).

be higher. Overall the values indicate a good reproducibility of the impregnation method.

Porosity data for the materials are reported in Table 2. The calcined original mesoporous γ -Al₂O₃ used as support has a surface area of 173 m² g⁻¹ with a narrow pore diameter distribution centred at 10 nm. All the catalysts display similar values of surface area, slightly lower than the surface area of the non-impregnated Al₂O₃ support (Fig. 3A). The values for the catalysts are in the range of 157–168 m² g⁻¹ of surface area and pore diameter centred at 9.6-10.2 nm. As expected the addition of metals leads to a slight diminution of the porosity, but it is noticed that the pore diameter distribution remains monomodal and very narrow (Fig. 3B). The surface and porosity analysis performed on the spent materials after reaction (Fig. 3C) all exhibit a similar decrease of the total surface area (\approx 8%), due to carbon coke deposition (Table 1). No changes in pore diameter are seen between fresh and spent materials (Fig. 3D) meaning that the majority of the pores are still accessible and have not been clogged by the carbon coke formed.

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Surface area and porosity analysis.

Material	BET surface area (m ² /g)	BJH _{des} pore diameter (nm)	BJH _{des} pore volume (cm ³ /g)	Spent material surface area (m ² /g)
Al ₂ O ₃	173	10.0	0.61	
Cat-Ref	168	10.2	0.57	151
Cat-In[0.25]	165	10.0	0.53	153
Cat-In[0.5]	162	9.8	0.53	149
Cat-In[0.75]	157	9.6	0.52	147
Cat-In[1]	162	9.7	0.52	152

The analysis of surface acidity was performed on the catalysts and on the calcined support via desorption of NH₃ and the results are shown in Fig. 4. The curves have been integrated dividing the desorption in three zones: the first one attributed to weak acid sites (0-250 °C), the second attributed to medium acidic sites (250-350 °C) and the third one to the strong acid sites (350-600 °C). Those values of ammonia desorption temperatures are similar to previous reports in the literature that are normally around 150-300 °C for weak-mild acid sites and 300-400 °C for strong acid sites [38,39]. According to the integrated area values for the desorption curve the trend of materials total acidity can be described as follows: Cat-In[0.25] > Al₂O₃ > Cat-Ref > Cat-In[0.5] > Cat-In[0.75] > Cat-In[1]. This trend shows how, with the exception of Cat-In[0.25], indium addition reduces the total acidity of the catalyst. Furthermore if the population of the strong acid sites is considered, a trend is observed that is proportional to the In loading: Al₂O₃ > Cat-Ref > Cat-In[0.25] > Cat-In[0.5] > Cat-In[0.75] > Cat-In[1]. This diminution of the population of strong acid sites, as also reported by Jahel et al. [39], is probably due to the formation of In aluminates during the thermal treatment steps of the synthesis, leading to the neutralisation of some acidic sites on the alumina support. This hypothesis is supported by H₂-TPR analysis (Fig. 5A), which shows higher hydrogen uptake in the high temperature zone (600-800 °C) that could be related to the formation of indium-aluminate species. The total acidic sites decreasing with the addition of In is in agreement with the experimental results of Liu et al. [40], Passos et al. [41] and Rodríguez-González et al. [42]. Those results suggests that the loading of indium component can partly neutralise the acid sites, especial the stronger acid sites of support and therefore in terms of reactivity it is expected that the indium-containing catalysts should be more selective towards dehydrogenation reducing undesired cracking reactions.

The profiles of reduction under hydrogen for the catalysts are reported in Fig. 5 and show three different zones of hydrogen uptake: a first well designated region, centred at 250°C, a second in the range of 350–540 °C and a third at higher temperature (550-800 °C) that is present only for the catalyst with high indium content (Cat-In[0.5], Cat-In[0.75], Cat-In[1]). In accordance with the results reported in the literature, the first peak is attributed to the reduction of Pt oxides and/or an oxy-chloro-platinum surface complex $[PtO_xCl_y]$ and, possibly, to the reduction of Sn oxide. The reduction of surface platinum takes place in the range 150-200 °C, Pt species in a stronger interaction with the support can reduce at higher temperatures (200-300 °C) [39,43], while reduction of Sn(IV) to Sn(II) can also contribute, as is reported to take place at (200-300°C) in presence of Pt catalysing the reduction [27]. The presence of indium is indicated by the increase of the first peak area, particularly accentuated when passing from the concentration (w/w) of 0.25% to 0.5%. This change in the profile can be attributed to reduction of a fraction of In oxide shifted at lower temperature due to a close Pt-In interaction (possibly forming Pt_xIn alloys), or an effect of indium reinforcing the Pt-Sn interaction and leading to a higher amount of Pt_xSn alloys. This hypothesis is in



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Fig. 3. Nitrogen adsorption/desorption isotherms (A and C) and pore diameter distribution (B and D) for the fresh and spent materials.

agreement with the results obtained by Jahel et al. [39] using Mössbauer spectroscopy, showing that with the increase of the indium content the signal related to Pt_xSn alloys also augments. The second zone of hydrogen uptake at 380–400 °C with a shoulder at 450 °C is interpreted as the reduction of Sn and In oxides competing with each other: reduction of In oxide on Al_2O_3 should take place around 430 °C while Sn oxide in strong interaction with the support at about 550 °C; the fact that both are shifted towards lower temperatures could be due to competition for reactive alumina sites, resulting in a weaker interaction with the alumina therefore an easier reduction [39]. The third zone of hydrogen uptake (550–800 °C) that is present only for the catalysts with In content higher than 0.25% is ascribed to the reduction of indium-aluminate species.

The values of metal dispersion and average metal particle size are calculated from the H_2 chemisorption analysis and are reported in Table 1. The dispersion obtained is similar for all the samples (45–50%) except for Cat-In[1] that displays a lower value (36%). Those values are an index of the accessibility of Pt atoms and indicate that a high indium loading decrease the amount of H_2 chemisorpted by geometric effects or alloy formation. The dispersion values are in good agreement with the catalyst activity with







Fig. 5. H₂-TPR profiles of the fresh materials (A) and an example of peak deconvolution (B).



Fig. 6. Hydrogen productivity evolution during reaction.

the highest value corresponding to the most performing catalyst Cat-In[0.5]. The calculated average particle size is in the range 2.3–3.2 nm. It has to be considered though, that the main factor responsible for hydrogen adsorption at room temperature in chemisorption measurements is the fraction of unalloyed Pt, rather than the Pt in alloy with Sn. As a consequence, it is difficult to tell whether the small differences between dispersion values are caused by a different amount of Pt-Sn alloy or by the actual particle size [43].

3.2. Catalytic testing results

Catalyst testing results reported in Fig. 6 show the evolution of hydrogen productivity relative to reaction time. The hydrogen production during the first 45 min is not shown as the equilibrium in the catalytic system is not reached; therefore, the values are not representative of the actual activity at time zero. Hydrogen productivity is expressed in litres at normal conditions for each hour of reaction per kg of catalyst (NL h^{-1} kg⁻¹).

The reactivity of the catalysts is a combined effect of the activity of metal sites (that catalyse the dehydrogenation reactions) and the acid sites (isomerisation, cyclisation reactions on weak-mild acid sites and cracking reactions on strong acid sites) [44]. Overall the materials activity may be described as follows: the catalyst that presents highest hydrogen yield is Cat-In[0.25], nevertheless the best compromise between hydrogen productivity, and purity, and catalyst stability is given by Cat-In[0.5]. The catalysts having highest indium content (0.75% and 1%) show enhanced stability with respect to the reference catalyst Cat-Ref, but the hydrogen productivity decreases. As suggested also by Benitez et al. [45] in a previous study on trimetallic catalysts, this effect could be caused by an excessive loading of indium that partially occludes platinum particles, limiting reactant accessibility to the active dehydrogenation sites.

Table 3

Materials performance and catalytic properties.

Comparing data derived from NH₃-TPD (Fig. 4) and catalyst testing results (Fig. 6) it is noted that lower H₂ productivity is associated with the diminution of weak-mild acid sites; those, together with Pt sites, can catalyse dehydrocyclisation of linear paraffins [46], leading to the formation of cyclic hydrocarbons and subsequently to H₂ and aromatics [23], explaining the correlation between indium content and productivity. It has been observed that, with exception of Cat-In[0.25] where there is an increased number of weak-mild acid sites, addition of higher amounts of indium leads to diminution of acidity; this effect together with the hindering effect of Pt particles by Sn and In could explain the trend in H₂ productivity for these materials.

Similarly, comparing H₂-TPR profiles (Fig. 5) and the productivity (Fig. 6), it is also observed that increased In loading leads to a stronger interaction between Pt and Sn (probably with formation of more Pt alloys) (Section 3.1), which could explain why indium addition enhances catalysts stability: there is much evidence in the literature showing that interaction between Pt and Sn leads to a more stable catalyst because of geometric and/or electronic effects [27,47,48]. Particles of Sn can help the separation between Pt clusters increasing the selectivity towards the dehydrogenation reaction and reducing particle sintering. The electron mobility between Pt and Sn could also modify the bond energy between Pt and adsorbed hydrogen. The relative lifetime of the catalysts is consistent with this hypothesis.

The hydrogen produced by PDh on kerosene has a very high purity that varies between 97.2% and 98.2%. CH₄ is the main byproducts, as well as traces of C₃ light hydrocarbons (Table 3). Contrary to what was expected, a slight increase of methane was noticed for the catalysts with a lower content of strong acid sites, in which case the hydrogenolysis reactions should decrease; however, the error on the quantity of C₃ could be considerable because the amounts were very close to the detection limit of the instrument (\approx 0.1%). The H₂ flow produced is CO free, with the implication that it should be possible to be fed directly to a PEM (proton exchange membrane) fuel cell system without further purification steps, leading to a good efficiency in the conversion to electric energy. A summary of the performance of the catalyst can be found in Table 3.

3.3. Carbon coke characterisation and study

Carbon coke deposition is the main reason for catalyst deactivation during the reaction of partial dehydrogenation of low sulfur jetA-1. Different techniques were used to investigate how indium addition influences the mechanisms of carbon formation leading to active phase deactivation. TGA/DTA, elemental analysis and Raman spectroscopy analysis results were compared with the purpose of having a more precise model of the deactivation phenomena.

All the analyses were performed on spent materials after a 6 h reaction time in order to evaluate the quantity and the nature of the carbon coke formed. The procedure for unloading the catalyst from the reactor was the following: kerosene vapour flow was stopped while an equal volumetric flow of Ar was turned on; after purging the system of kerosene residues, the simulated recycle of H_2 and the heating of evaporator, pre-heater and reactor were turned off.

Material	Lifetime (h) ^a	Deactivation (%) ^b	H ₂ purity (%)	H ₂ yield (%)	H ₂ /kerosene (NL/L)	$TOF(s^{-1})$
Cat-Ref	34.8	16.5	98.2	5.7	79.5	0.58
Cat-In[0.25]	48.9	13.9	98.1	6.5	88.1	0.73
Cat-In[0.5]	107.1	11.8	97.8	6.4	86.7	0.69
Cat-In[0.75]	43.6	17.4	97.4	5.5	76.3	0.63
Cat-In[1]	52.4	14.0	97.2	5.5	76.7	0.59

^a Linear extrapolation (180–360 min TOS).

^b Ratio initial/final H₂ productivity.

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Table 4	
Carbon coke	characterisation

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Material	TGA/DSC coke (%)	Coke 1st peak area (a.u.) ^a	Coke 2nd peak area (a.u.) ^a	E.A. total (%)	E.A. carbon (%)	E.A. hydrogen (%)	E.A. C/H	Ordered/ disordered coke ^b
Cat-Ref	3.2	12.3	6.9	3.0	2.4	0.6	4.0	0.68
Cat-In[0.25]	3.0	11.8	10.2	2.9	2.3	0.6	3.8	0.61
Cat-In[0.5]	2.6	10.5	7.6	2.7	2.1	0.6	3.5	0.56
Cat-In[0,75]	2.1	10.8	7.4	2.0	1.4	0.6	2.3	0.44
Cat-In[1]	2.1	11.4	5.5	2.0	1.4	0.6	2.3	0.47

^a Deconvolution of DTA signal.

^b Deconvolution of Raman signal.



Fig. 7. DTA signal evolution recorded during TG analysis of the spent catalysts (A) and an example of peak deconvolution (B).

When the system had cooled down the catalyst was discharged and degassed to eliminate absorbed kerosene.

Table 4 lists the amount of carbon coke formed during the reaction obtained for the spent catalysts. Indium addition has a beneficial effect, reducing the amount of carbon deposited during the reaction even when it is present in small amounts. From the differential thermal analysis plot (Fig. 7) it may be observed that the exothermic peaks of coke combustion seem to be the result of two different contributions, with a peak at lower temperature (300-350 °C) and one at higher temperature (400-450 °C). After deconvolution and integration of the two contributions, a linear correlation emerged between the area of the first peak and catalyst lifetime, while the second peak seems to be related to the acidity of the material. In line with previous studies on carbon coke deposits [49,50], we assume that the first peak is related to coke formed on the active metal phase and the second peak to coke formed on acid sites of the alumina support. The first type of carbon burns at lower temperature because its oxidation is promoted by the proximity of Pt particles and it is the major factor for catalyst deactivation as this carbon "covers" the active phase. The second type of coke is in strong interaction with the support and burns at a higher temperature; it affects the deactivation much less because it does not interact directly with the active phase. However, it could hinder access to active sites by pore and channel clogging, but, as seen from catalytic tests and porosity analysis on spent materials, the amount of carbon seems to be insufficient to produce such an effect. The effect of indium is then to diminish the quantity of carbon coke formed on the active phase, thus increasing the lifetime of the catalysts. It has also been hypothesised that the presence of indium can facilitate the migration of the carbon from the active phase towards the support, helping this way to keep the active sites reactive. There



Fig. 8. Raman spectra of the spent catalysts (A) and an example of peak deconvolution (B).

is evidence in the literature of coke migration from the active metal to the support for bimetallic Pt catalyst [51]. In particular Vu et al. [52] observed that carbon coke mobility on the catalyst surface of Pt-Sn/Al₂O₃ is related to the presence of different Pt_xSn alloys. As noticed from H₂-TPR analysis (Section 3.1) the presence of indium seems to increase the amount of Pt_xSn alloys formed, which suggests that the effect of coke migration from the active phase to the support could contribute to the better stability of indium doped catalysts.

CNHS elemental analysis results, listed in Table 4, are in good correlation with the values obtained by TG analysis giving a confirmation on the reliability of the carbon coke study. No trace of sulfur was found in the deposit and the graphitisation of the coke calculated as ratio between C/H (w/w) is proportional to the total amount of coke formed.

In order to complete the study of the carbon coke formed during PDh reaction, Raman spectroscopy has been performed on the spent catalysts. This technique presents some difficulties related to interference by fluorescence caused by some aromatics and polyaromatics present in the carbon, but with a fine tuning of the instrument parameters the spectra reported in Fig. 8 were obtained. For the catalysts containing a high amount of coke (Cat-Ref, Cat-In[0.25]) the peaks related to ordered carbon D1 (1350 nm) and G (1590 nm) are clearly visible, while other peaks decreased. The ratio between ordered and disordered carbon has been calculated as the ratio between the area of D1 + G peaks and the other peaks [53] obtaining a good correlation with the graphitisation ratio previously calculated from elemental analysis data (Table 4).

4. Conclusions

The effect of addition of indium to the well known system based on Pt-Sn/Al₂O₃ has been investigated. The reducibility of the active phase is improved and the activity towards the dehydrogenation reaction is increased. The number of strong acid sites is reduced, so avoiding undesired side reactions such as cracking, and consequently decreasing carbon coke formation and improving catalyst stability. The presence of indium also diminishes the amount of coke formed in the proximity of Pt particles, which serves to stabilise the catalyst activity. The catalyst Cat-In[0.5] with metal ratio of 0.5:1:1 In:Pt:Sn has been identified as the best compromise between catalyst activity and stability. This catalyst allows the production of a hydrogen flow (purity 97.8%) of 2900 NL h⁻¹ kg_{cat}⁻¹ corresponding to 86.7 NL $L_{kerosene}^{-1}$ that can generate around 2.9 kW electricity (assuming a 50% efficiency for PEM fuel cell). The hydrogen yield is about 6.5% and is generated mainly from dehydrogenation of cycloalkanes to aromatics. This degree of conversion should allow the utilisation of partially dehydrogenated kerosene as combustible fuel.

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2.4.5 Deposition of Pt/Sn on a new sucrose templated γ-alumina: characterisation, activity and study of the active sites

The Pt-Sn/ γ -Al₂O₃ material JM1, prepared at Johnson Matthey using as support an alumina from Sasol (SCFa140), was one of the first and most promising materials for kerosene partial dehydrogenation, identified during the initial studies of the "GreenAir" project. In Chapter 2.4.1 it was also highlighted that Pt-Sn on a modified γ -Al₂O₃ (JM2), obtained by a method easy to scale-up, seems to be the most promising catalyst. As consequence, in order to reach a higher and stable catalytic activity, a novel, low cost and easy to scale-up γ -Al₂O₃ support has been developed and optimised. This synthesis uses sugar (sucrose) as template following the methodology described in Chapter 2.1.2, based on the work of Xu et al. [28]. Two new supports, differing by the aluminium/sucrose ratio, have been used for the preparation of Pt-Sn catalysts (ALUSUC1[PtSn], ALUSUC2[PtSn]).

At an early stage of the work, the material ALUSUC1 have been synthesised with a molar ratio between the sucrose template and the aluminium precursor of 1:1 and this support has been used for the deposition of Pt-Sn by incipient wetness impregnation to obtain ALUSUC1[PtSn]. This catalyst has been developed in collaboration with doctor Reyes-Carmona (University of Montpellier 2) and the results of the characterisation have been fully reported in his PhD thesis [38] and in the publication on "Catalysis Today" volume 210 (2013) pages 26–32 [39]. Here we report briefly the main characteristics (porosity, acidity and metal dispersion) of this catalyst, compared to the same characterisation of JM1 (Table 9).

	Surface area (m ² ·g ⁻¹)	Pore diameter (nm)	Surface acidity (µmol _{NH3} ·g ⁻¹)	Metallic dispersion (%)
ALUSUC1[PtSn]	153	7.5	273	69
JM1	133	9.8	120	53

Table 9 - Summary of the characterisation of ALUSUC1[PtSn]

In an extension of this work the support ALUSUC2 have been synthesised following a similar same route, but with a modification of the molar ratio between the sucrose template and the aluminium precursor to 0.5:1 instead of 1:1. In this chapter the results obtained with the Pt-Sn/ γ -Al₂O₃ material ALUSUC2[PtSn] will be discussed and compared to the results obtained with the catalyst ALUSUC1[PtSn], in order to explain how the different characteristics of the material affect the performances of the PDh of kerosene.

> Characterisation of the ALUSUC2[PtSn] catalyst

The surface and porosity analysis performed on ALUSUC2 and ALUSUC2[PtSn] catalyst obtained after the metals deposition, are reported in Fig. 16-17:







Figure 17 - Pore size distribution of JM1, ALUSUC1 and ALUSUC2 materials

The surface area of ALUSUC2[PtSn] (226 m²·g⁻¹) is higher than that of the reference JM1 (133 m²·g⁻¹) and that of ALUSUC1[PtSn] (153 m²·g⁻¹), showing an enhancement of the porosity despite the diminution of the quantity of sucrose template used for the synthesis. For ALUSUC1[PtSn] the distribution of pore is large and slightly shifted towards larger pores. The maximum of the distribution is at 7.5 nm for the support alone (ALUSUC1) and 11 nm for the metal supported catalyst (ALUSUC[PtSn]). This distribution of pores is relatively close to that of the catalyst JM1. The pore size distribution for ALUSUC2 and the supported catalyst ALUSUC2[PtSn] are very similar and the maximum of the distribution (4.5 nm) correspond to a much smaller diameter than that of ALUSUC1, ALUSUC1[PtSn] and JM1.

The ALUSUC2 support and ALUSUC2[PtSn] catalyst have been analysed via NH_3 -TPD and H_2 -TPR in order to obtain further information on the materials. The results collected are shown in Fig. 18-19.



Figure 18 - NH₃-TPD profiles of ALUSUC2 and ALUSUC2[PtSn]



Figure 19 - H₂-TPR profile of ALUSUC2[PtSn]

The NH₃-TPD profiles indicate a diminution of the total acidity after the Pt and Sn impregnation. The acidity of the ALUSUC2[PtSn] material is overall lower respect the values measured for ALUSUC1[PtSn] synthesis passing from 273 μ mol_{NH3}·g⁻¹ to 96 μ mol_{NH3}·g⁻¹. The acidity measured for the reference JM1 (120 μ mol_{NH3}·g⁻¹) is intermediate between the ones measured for the ALUSUC materials.

The reduction profile of ALUSUC2[PtSn] is composed by a main asymmetric peak of hydrogen uptake with a maximum at ≈ 250 °C. In general it is accepted that the overall profile results from three principal contributions: the main contribution is attributed to the reduction of Pt oxides and possibly to the reduction of Sn oxides. The reduction of Pt species in strong interaction with the alumina support are reported to be reduced at 200-300 °C [22,40]. The reduction of Sn(IV) to Sn(II) is reported to take place at 200-300 °C in presence of Pt catalysing the reduction, leading to the formation of Pt_xSn alloys [2,41,42]. The alloy formation is also corroborated by Mössbauer analyses on the catalyst that are reported later in this chapter. The hydrogen uptake observed above 350 °C, causing the asymmetry observed in the hydrogen uptake peak, is attributed to the reduction of Sn oxides in strong interaction with the support [41,42].

In order to obtain information on the metal dispersion, the ALUSUC2[PtSn] catalyst have been analysed by H₂-pulse chemisorption. The result obtained is reported in Fig. 20:



Figure 20 - H₂ pulse chemisorption on ALUSUC2[PtSn]

The metallic dispersion for ALUSUC2[PtSn] (88 %) is higher than that observed for JM1 (53 %) and ALUSUC1[PtSn] (69 %)

> Optimisation of the catalyst activation

Beside the improvement of the materials properties obtained by modification of the preparation steps, a further improvement has been made by optimising the procedure for the catalyst activation. The standard procedure for Pt, Pt-Sn, Ni and others dehydrogenation catalyst consists usually in a reduction carried out under a hydrogen flow. It has been noticed that the catalytic activity for the majority of the catalyst tested during the process show a consistent enhancement of the performances when a further thermal treatment is performed just before the reduction in hydrogen. This two-steps activation procedure, described in Chapter 2, has been analysed in details on the ALUSUC2[PtSn] catalyst in order to better understand the causes of this activity difference.

The increase of activity obtained with the new activation procedure, in terms of hydrogen productivity, can be observed in Fig 21. The reactions have been carried out at 450 °C, 1 MPa, $\tau = 2s$ and a 7% vol. hydrogen recycling, using LSK as reagent.



Figure 21 - Comparison between the activation methods using the catalyst ALUSUC[PtSn]

The reasons related to this change of activity caused by the different activation method have been studied by Mössbauer spectroscopy and presented in the next chapters.

Comparison between the activity of the catalytic materials in the partial dehydrogenation of kerosene

Modifying the conditions of the preparation of the support and the procedure of activation of the catalysts has a considerable effect on their activity. The hydrogen productivity of ALUSUC2[PtSn] is compared to that of ALUSUC1[PtSn], JM2 and the reference JM1 (Fig. 22).



Figure 22 - Hydrogen productivity compartison between the two ALUSUC[PtSn] catalysts

The hydrogen productivity increases from an average (over the period of reaction 360 min) below 1000 NL·h⁻¹·kg_{cat}⁻¹ for ALUSUC1[PtSn] to an average of 3500 NL·h⁻¹·kg_{cat}⁻¹ with ALUSUC2[PtSn]. The stability is also

consistently enhanced with almost a doubled lifetime with respect to the previous result. It is interesting to notice that the activity of the ALUSUC2[PtSn] is superior to the reference catalysts JM1, which is also a Pt-Sn/ γ -Al₂O₃. JM1 has a productivity around three times lower; JM2 that is a baseline catalyst (Pt-Sn supported on BaO modified alumina), has a productivity that is 1000 NL·h⁻¹·kg_{cat}⁻¹ lower with a slightly inferior lifetime compared to ALUSUC2[PtSn]. The DTA on the carbon coke formed during reaction for the ALUSUC1[PtSn] and ALUSUC2[PtSn] in comparison to the reference JM1 are shown in Fig. 23.



Figure 23 - TGA/DTA analysis comparison between ALUSUC1[PtSn], ALUSUC2[PtSn] and JM1

As the lifetime for ALUSUC2[PtSn] is almost doubled compared to ALUSUC1[PtSn], the amount of carbon coke deposited (after 6 hours reaction) is reduced of about a half, from 7 % wt. with ALUSUC1[PtSn] to 3.8 % wt. with ALUSUC2[PtSn]. JM1 also presents a higher amount of carbon deposit (5.1 % wt.) with respect to ALUSUC2[PtSn]. As the two reactions are performed using LSK the effect of sulfur on the deactivation is negligible. For ALUSUC1[PtSn] and JM1 catalysts the DTA signal is split in two

contributions: one at higher temperature (400-500 °C) and one at lower temperature (300-400 °C). It is important to note that the first peak area, at lower temperature, is considerably reduced for ALUSUC2[PtSn] with respect to JM1 and ALUSUC1[PtSn], almost observing the disappearance of the peak. According to previous studies on carbon coke deposits [43,44], it is proposed that the first peak is related to coke formed on the active metal phase and the second peak to coke formed on acid sites of the alumina support. Therefore, even though the second peak area is similar for the catalysts, the activity and the lifetime of ALUSUC2[PtSn] are enhanced because the carbon coke is deposited on support and not on the active metal sites.

Study of the effect of the activation steps on the catalyst by Mössbauer spectroscopy

In order to better understand the effect of the activation steps on the activity, the ALUSUC2[PtSn] material have been studied by ¹¹⁹Sn Mössbauer spectroscopy. This technique is able to measure the hyperfine interactions of the nuclei of a specific element (Sn in our case) with the surrounding environment, giving precise and useful information about oxidation states, magnetic hyperfine fields, coordination symmetry, and lattice vibrations. The ¹¹⁹Sn Mössbauer spectroscopy has been widely used for the identification and quantification of the different tin species present in supported bimetallic systems and recently Olivier-Fourcade et al. [22,45] tried to rationalize the large amount of data existing for the Pt–Sn couple to establish a accurate chart of hyperfine parameters, which is very useful to identify a large variety of tin species that occur on bimetallic Pt-Sn catalysts after oxidation or reduction treatment. The chart is reported in Fig. 24:



Figure 24 - Identification diagram of tin species found in PtSn/Al₂O₃ catalysts [29]

Different samples of ALUSUC2[PtSn] catalyst have been prepared and analysed by ¹¹⁹Sn Mössbauer (MsB) spectroscopy in order to gather information on the environment of Sn at different stages of the activation procedure: the first stage is the catalyst as synthesised (As synth), the second stage is the catalyst as synthesised and activated with a one-step activation procedure by reduction in hydrogen flow (As synth + Red), the third stage is the catalyst after an additional thermal treatment (Thermally treated 500 °C, 2 h), the fourth stage is the catalyst thermally treatment followed by reduction in hydrogen (Thermally treated + Red) and the fifth stage is the spent catalyst after 6 hours PDh reaction on LSK, with the fully activated catalyst. For the Mössbauer characterisation the same amount of catalyst, from the same batch, has been used. The values of isomer shift (IS), quadrupole splitting (QS), full width at half the maximum (FWHM) are reported in Table 10.

ALUSUC[PtSn]	IS δ (mm·s⁻¹)	QS∆(mm·s ⁻¹)	FWHM	PHASE ¹	CONTRIBUTION.
As synth	0,00	0,62	1,01	SnO ₂ 1	100
Thermally	0,12	0,50	0,86	SnO ₂ 1	47
treated	0,21	1,23	0,86	Sn ^{IV} 2	53
	0,06	0,48	0,92	SnO ₂ 1	30
Thermally	0,00	0,91	0,92	Sn ^{///} 2	28
treated + Red	1,27	0,83	0,92	Pt _x Sn(O)	23
	3,15	1,83	0,92	Sn [″] 2b	19
	0,04	0,42	0,87	SnO ₂ 1	26
As synth +	0,01	0,85	0,87	Sn ^{IV} 2	31
Red	1,34	0,78	0,87	Pt _x Sn(O)	26
	3,23	1,75	0,87	Sn [″] 2b	17
Spent	0,00	0,56	0,94	SnO ₂ 1	78
opent	1,74	1,41	1,20	Pt _x Sn(O)	22

Table 10 - ¹¹⁹Sn Mossbauer spectroscopy hyperfine parameters for ALUSUC2[PtSn] samples

¹According to diagram reported in Fig. 24

In Fig. 25 is presented a representative series of Mössbauer spectra showing the evolution Sn phases at different steps: as synthesised, during the two-steps activation and after PDh reaction:


Figure 25 - ¹¹⁹Sn MsB spectra evolution for the ALUSUC2[PtSn] catalyst

The "As synthesised" sample has been obtained after calcination at 560 °C during 5 hours. Sn is present only in the phase SnO_21 and after a further thermal treatment in air (Thermally treated), the formation of a second Sn phase is observed, labelled $Sn^{IV}2$ in Mössbauer analysis. The SnO_21 phase is a Sn^{IV} phase consisting in a lattice with Sn-O-Sn bridges, while the $Sn^{IV}2$, that

have an higher quadrupole splitting, consist in a different Sn lattice with Sn-O-M bridges (M = Al, Pt). The SnO_2 1 phase tend to form partially embedded particles in the alumina surface (Sn-O-Sn only), while the $Sn^{IV} 2$ phase would constitute the interfacial layer with the alumina bulk or the Pt particles (Sn-O-M interactions). The formation of the Sn^{IV} 2 phase after further thermal treatment suggests an increase in the interaction between the Sn particles with the support and/or the Pt. After the reduction in hydrogen (Ox-Red) the formation of two new Sn phases is noticed: one has been identified as $Sn^{II} 2b$ and the other as $Pt_xSn(O)$. The Sn^{II} phases can be classified in Sn^{II} 2a and Sn^{II} 2b: the first corresponds to a Sn^{II} oxide containing principally Sn–O–M bridges, while the latter is a Sn^{II} oxide with Sn-O-Sn bridges. In this case the Sn^{II} phase has been labelled as Sn^{II} 2b, but its quadrupole splitting lies in between the two phases (Sn^{II} 2a and Sn^{II} 2b) suggesting the possible presence of Sn-O-M bridge contributing to the signal. The $Pt_xSn(O)$ consists in an "oxometallic" form of PtSn alloy where the two metals are in loose contact with oxygen and Sn is partially embedded in the Pt cluster. This phase is characterised by a quadrupole splitting value different from zero. After reaction (Spent) the only two phases remaining are in SnO_2 1 and $Pt_xSn(O)$ [22,29,45].

In Fig. 26 are presented two Mössbauer spectra showing the difference of phase multiplicity between the catalyst after a simple activation by reduction and the catalyst thermally treated before reduction:



Figure 26 - ¹¹⁹Sn MsB spectra comparison between standard and optimised activation method

The immediate difference noticed between the two activation procedures, in terms of Sn phases formation, is the relative ratio between the SnO₂ 1 and Sn^{*IV*} 2. In the case of the two-steps activation procedure, after the thermal treatment (Thermally treated), is observed the formation of Sn^{*IV*} 2 is observed. This phase involves Sn-O-M bonds that, seems to favour the reduction of Sn to the phase Sn^{*II*} 2b. The amount of Sn^{*II*} 2b formed by reduction is greater on the thermal treated catalyst (Thermally treated + Red) than that obtained after a simple reduction without thermal treatment (As synthesised + Red). Even though the formation of Sn^{*IV*} 2 (indicating some amount of Sn-O-M interaction) take place earlier for the two-step activation procedure, the amount of Pt_xSn(O) formed after the reduction step is similar for both activation procedures, but an important difference is noticed in the quadrupole splitting value for the phase Sn^{*II*} 2b: in the case of the two-steps activation (Thermally treated + Red) the quadrupole splitting is in between the range attributed to Sn^{*II*} 2a and Sn^{*II*} 2b suggesting the presence of some Sn-O-Pt bridges, while for the material without additional thermal treatment the quadrupole splitting lies inside the range of Sn^{II} 2b suggesting the presence of Sn-O-Sn bridges only [45,46]. The difference measured on the amount and nature of the Sn^{II} phase formed, depends on the activation procedure and might be at the origin of the difference of activity: with the two-steps. The presence of Sn-O-Pt bridges seems to be beneficial to the catalytic activity in terms of hydrogen productivity and lifetime.

It is important to note that all the catalytic tests presented in this manuscript, have been performed using the two-steps activation method.

2.4.6 Rectification of kerosene Jet A-1 as treatment for increasing the efficiency in the catalytic partial dehydrogenation

The studies on the partial dehydrogenation of kerosene have been carried out mainly on a desulfurised type of Jet A-1 (LSK) with a maximum of 3 ppm of sulfur. The use of this kerosene is possible as it is commercially available, but is more expansive than standard Jet A-1 and the supply can't be assured in all areas of the world due to different legislations and environmental politics. Consequently in the prospective of a global development of such a hydrogen delivery system it would be convenient to work with standard Jet A-1.

The thermal fractionation by rectification is a well-known successive distillation process for separation of components with similar boiling temperatures, commonly found in refineries and chemical industries. It is expected from the fractionation to select a range of components more suitable for the partial dehydrogenation, in particular it is known that naphtene are more amenable to dehydrogenation than paraffins. In addition the rectification process could possibly lead to lower sulfur content in a kerosene fraction taking a certain amount of the head product of the distillation which has a lower boiling range. The sulfur components found in kerosene are usually benzothiophenes and its derivatives [47].

> Kerosene Jet A-1 rectification and analysis of the fractions chemical composition

The fractionation of commercial Jet A-1 (228 ppmw S) has been carried out in a laboratory scale Vigreux rectification column at the German Aerospace Center (Deutsches Zentrum für Luft und Raumfahrt DLR). Three different kerosene fractions have been prepared for the partial dehydrogenation process by loading the raw kerosene in the boiler and taking the 5 %, 14 % and 32 % wt. as the rectification head product, taking each fraction from a new raw charge. In Fig. 24 are shown the boiling point curves for the fractions and the standard Jet A-1:



Figure 27 - Boiling point curves for Jet A-1 kerosene and its fractions

The composition of the Jet A-1 and its fractions was studied with a GC-MS (Thermo T230L Trace DSQ Turbo 250L sec 230) identifying around 300 peaks depending on the kerosene sample analyzed. The compounds are classified on the base of the chemical structure: iso-paraffins, n-paraffins, cyclic, dicyclic, aromatic and diaromatic hydrocarbons. The sulfur content in fractions was analyzed using an elemental analyzer (AnalytikJena/multi EA 5000). The composition of kerosene Jet A-1 and its fraction are shown in Fig. 25 and Fig. 26:



Figure 28 - Chemical distribution of kerosene Jet A-1 and its fractions

The Jet A-1 kerosene is a complex mixture of hydrocarbons with a chain length in the range of C_8 - C_{15} with a weighted average centred on C_{11} . The fractions obtained by rectification have lower boiling point and therefore present a lower carbon chain length: the weighted average is C_8 - C_9 , C_9 - C_{10} and C_{10} for the 5%, 14% and 32% fraction respectively.



Figure 29 - Composition of kerosene Jet A-1 and its fractions

One important result of Jet A-1 rectification is the reduction of S content in the fractions: from the 228 ppm of the Jet A-1 the sulfur decreases to 4 ppm in the 5% fraction, 12 ppm in the 14% fraction and 24 ppm in the 32% fraction. Another noticeable change is the concentration of the cyclic hydrocarbons, aromatics and paraffins: going towards lighter fractions the paraffins and aromatics content decrease while the cyclic hydrocarbon content increases.

> Partial dehydrogenation of fractionated kerosene

The kerosene fractions and a standard Jet A-1 fuel (used as reference) have been tested using JM2 as catalyst. The catalytic reactions were carried out at 1 MPa, 450 °C, $\tau = 2s$ and were repeated twice for each fraction showing a good reproducibility. The evolution of the productivity with time is shown in Fig. 27:



Figure 30 - Evolution of hydrogen productivity curves for Jet A-1 fractionations over a period of 6 h

The hydrogen productivity for the three kerosene fractions is higher than that of =Jet A-1 with the 5% fraction displaying the highest productivity. A marked difference in productivity is also noticed between the 32% fraction and the 14% fraction. In order to explain these different behaviours the compositions of the fractions after reaction have been determined. The composition of the fraction after the test is compared to that of the initial fraction in Fig. 28:



Figure 31 - Comparison between the composition of kerosene fraction before and after reaction

The amount of paraffins and iso-paraffins do not change during the reaction and the amount of cyclic hydrocarbons is the most reactive in the reaction. Cyclic hydrocarbons are completely dehydrogenated to form aromatics: the diminution of the quantity of cyclic hydrocarbons corresponds to the increase of the amount of aromatics.

Sulfur compounds are almost completely eliminated during the reaction. Sulfur is a well-known poison for Pt catalyst so there is the possibility that the sulfur contained in the kerosene is retained on the catalyst. Elemental analysis performed on the spent catalysts has shown the presence of sulfur, but in a less quantity that initially present in the fraction. Part of the sulfur could have been removed from the liquid in the form of H_2S , but no peak related to H_2S is detected by GC in the produced gas stream.

The purity data related to the hydrogen produced in the course of the reaction have been measured for each fraction. The data of hydrogen purity and the main impurities present in the gas outflow are presented in Table 11:

	H ₂ (%)	CH ₄ (%)	C ₂ -C ₄ (%)
5% Fraction	99,0	0,9	0,1
14% Fraction	98,8	1,1	0,1
32% Fraction	98,6	1,2	0,2
Jet A-1	98,6	1,1	0,3

 Table 11 - Hydrogen purity from PDh of kerosene fractions

Hydrogen purity decreases when the weight fraction increases, with the highest value of 99.0% for the 5% fraction. This effect could be due to both the different amount of sulfur in the liquid and the different composition in hydrocarbons. Overall the values are high and show an improvement of the purity of the hydrogen produced after the rectification process.

Characterisation of spent materials, discussion on the causes of the deactivation and conclusions

The spent catalyst charge used for each reaction have been analysed via TG/DTA and EA in order to obtain information regarding the type of carbon coke formed on the material. A summary of the results is presented in Table 12:

	-	Elemental Analysis		TGA
	C %	Н %	S %	Coke %
5% Fraction	0,98	0,36	0,064	1,1
14% Fraction	1,06	0,38	0,070	1,1
32% Fraction	1,73	0,37	0,093	1,9
Jet A-1	2,94	0,44	0,104	3,4

Table 12 - Carbon coke analysis on spent catalyst after PDh of kerosene fractions

Carbon coke analysis performed by EA and TGA show consistent results between the two techniques. The quantity of carbon coke increases with the fraction weight: 5% Fract. < 14% Fract. < 32% Fract. < Jet A-1. The sulfur present on the spent catalysts measured by EA increases with the amount of sulfur present in the fraction. The deactivation is caused by the two effects of carbon deposition and sulfur poisoning. The carbon deposition depends on the nature of the hydrocarbon in the composition of the fraction, while the sulfur poisoning is directly related to the amount of sulfur present in the fraction. Using the results of EA it is possible to calculate exactly how much sulfur is deposited on the spent catalyst and to compare it to the total amount of sulfur present initially in the fractionated fuel. The results of the calculations are shown in Table 13.

	Sulfur Pumped (mg)	Sulfur on spent Cat. (mg)
5% Fraction	0,54	0,59
14% Fraction	1,55	0,70
32% Fraction	2,93	0,81
Jet A-1	29,50	1,05

Except for the reaction with the 5 % fraction, not all the sulfur introduced in the system is retained in the catalyst. In Fig. 29 is shown the comparison between the sulfur retained on the catalyst as function of the sulfur content in the liquid fraction before reaction:



Figure 32 - Sulfur retention on catalyst as function of sulfur in the fraction

It is known that, under the appropriate operative conditions, Pt/γ -Al₂O₃ is an efficient deep hydrodesulfuration (HDS) catalyst and that even his sulfided correspondent PtS is active in the HDS reaction presenting similar or higher activity as the well known catalytic systems based on CoMo sulfides and NiMo sulfides [48]. The fact that the sulfur contained in the kerosene fractions is completely eliminated during the reaction proves that HDS reaction takes place in PDh reaction conditions as well. The amount of sulfur retained on the spent catalysts can be attributed in minor part to sulfur containing hydrocarbons that remain in the pores after the reaction, but the majority of the sulfur probably originates from the PtS and SnS₂ formed during reaction. The sulfidation of Pt is a partially reversible process: with the exception of a small amount of S that is irreversibly absorbed by Pt causing poisoning, PtS is instable under hydrogen pressure and the amount formed depends on the concentration of S and H₂ in the reaction atmosphere [48,49]:

$$PtS_{(s)} + H_{2(g)} \leftrightarrow Pt^{0}_{(s)} + H_{2}S_{(g)}$$

The formation of SnS_2 also gives a considerable contribution to the quantity of sulfur retained on the spent catalyst, having a higher chemical affinity for sulfur than Pt. The heat of formation of SnS_2 and PtS_2 are -40 kcal·mol⁻¹ and -26 kcal·mol⁻¹ respectively [50].

During the PDh reaction the Pt-Sn catalyst activates both the dehydrogenation and the hydrodesulfuration reaction and the sulfur contained in the liquid fraction is released in the form of H_2S , moving the equilibrium of the former equation to the left. The amount of sulfur retained in the catalyst is therefore proportional to the quantity of sulfur contained in the liquid. The H_2S released in course of reaction has not been detected by GC analysis and, even though a small diminution of the hydrogen purity has been measured with the increasing of the sulfur content in the fraction, it is possible that the H_2S is not detected by GC because it is under the detection limit. Assuming that all the sulfur not retained in the catalyst is released in form of H_2S , from

the sulfur balance (Table 13) it has been calculated the volumetric % of H_2S in the hydrogen outflow. This value is zero for the 5 % fraction because all the sulfur contained in the liquid is retained on the spent catalyst, while for the 14 % and 32 % fractions the H_2S concentration in the produced gas is 0,007 % vol. and 0,026 % vol. respectively.

The presence of sulfur in the outflow though very low, might cause the deactivation of the fuel cell catalyst and in order to utilise this system a sulfur trap might be placed after the reactor to optimise the total efficiency of the system, for example a ZnO based sulfur adsorber [51,52]. However fractionation of kerosene Jet A-1 would allow the use of standard Jet A-1 kerosene instead of a LSK, avoiding the problem of sulfur poisoning of the catalyst for the PDh reaction.

This study has been carried out in collaboration with the Deutsches Zentrum für Luftund Raumfahrt (DLR) German Aerospace Center, Institute of Technical Thermodynamics Thermal Process Technology, Pfaffenwaldring, Stuttgart, Germany which performed the kerosene fractionation and GC-MS analysis.

2.5 References

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3. Hydrogen generation via partial dehydrogenation of gasoline and diesel

The studies on kerosene derived from the founding idea of the "GreenAir" project with the objective of feeding a fuel-cells APU on- board an airplane. The results obtained in the catalytic partial dehydrogenation of this fuel are very promising for a future application. The study of the feasibility of using a similar APU for other types of vehicles as trucks, boats and ships is also of interest, but the adaptation of this technology to other vehicles requires another investigation on the possibility of carrying out the catalytic partial dehydrogenation with other fuels as feedstock, such as gasoline and diesel.

3.1 Experimental part

3.1.1 Description of the catalytic material and characterisation techniques

The catalytic material ALUSUC2[PtSn], containing 1% Pt-1% Sn supported on a sucrose templated γ -alumina, has shown promising results for the partial dehydrogenation of kerosene. For this reason this catalyst has been chosen for the study of the partial dehydrogenation of diesel and gasoline surrogates. A detailed description of the ALUSUC2[PtSn] preparation and characterisation can be found in Chapter 2.1.2 and 2.4.5 respectively.

The characterisation techniques employed for the analysis on the material are the same as described in Chapter 2.2.1. The test rig also used for the PDh of kerosene is described in Chapter 2.3.1. The description of the operational procedures for the catalyst activation and the method used for the calculation of hydrogen productivity, conversion and selectivity can be found in Chapter 2.3.1 and 2.3.2 respectively.

3.1.2 Description of the gasoline and diesel surrogates used as feedstock

The most common petrol fractions used as combustible in naval and road transportation are diesel and gasoline. The diesel is heavier than kerosene and it contains usually a range of hydrocarbons with distribution centred on C_{16} , while gasoline has lighter hydrocarbons with a distribution centred on C_8 . The different composition of these two fuels compared to the kerosene, together with the different amount of sulfured compounds, will probably change the reactivity and the optimal parameters for the catalytic partial dehydrogenation reaction.

In the present preliminary study, the feasibility of the PDh of gasoline and diesel have been investigated using four different fuel surrogates as feedstock and comparing the results to the ones obtained with a kerosene surrogate, in order to evaluate the hydrogen productivity and the differences in the reactivity. This investigation consists in a screening of temperature, pressure and a study of the effect of hydrogen recycling for the surrogate tested. A first evaluation of the reaction mechanisms and deactivation is also included.

The use of a five components surrogate instead of the real fuel have the advantage of simplifying the study of the reactivity and the calculation of the conversions for the different classes of compound, that would be very difficult using real gasoline and diesel because of the variety of hydrocarbons and the presence additives that they contain. The surrogates have been chosen in order to be the most representative as possible of the fuel, both in terms of chemical composition and in thermodynamic properties. A kerosene surrogate have been formulated during the preliminary studies of the "GreenAir" project to represent the LSK. Gasoline surrogate B, formulated by Pera et. al. [1], has been selected as the best model for gasoline, while gasoline surrogate A is a variation of the surrogate B with addition of a small amount of ethanol in order to better represent new generation gasoline. As a model for a diesel fuel,

a surrogate mixture proposed by Pitz et. al. [2] has been selected. A second diesel surrogate has also been characterised in order to study the effect of different types of naphtenes on catalyst deactivation. The composition of the surrogates is reported in Table 1.

Surrogate	Compound (% vol.)					
Kerosene	Dodecane	Me-cyclohexane	T-butylbenzene	Decalin	Tetralin	
Kerösene	65	14	10	6	5	
Gasoline A	N-heptane	lso-octane	Cyclo-hexane	Cyclo-hexene	Toluene	Ethanol
Gasonine A	13,5	37,5	9	6	30,5	3,5
Gasoline B	N-heptane	Iso-octane	Cyclo-hexane	Cyclo-hexene	Toluene	
	15	38	10	7	31	
Diesel A	N-hexadecane	lso-octane	Butyl-cyclohexane	Butyl-benzene	1-Me-naphtalene	
Dieserri	24	19	27	23	7	
Diesel B	N-hexadecane	Iso-octane	Butyl-cyclohexane	Butyl-benzene	Tetralin	
Dieserb	24	19	27	23	7	

Table 1 - Fuel surrogates composition

3.1.3 Calculation of the bubble and dew point for the surrogate mixtures

The temperature of the evaporator needs to be high enough for the complete evaporation of the liquid mixture, but not too elevated in order to avoid thermal cracking and decomposition of the molecules before reaching the catalytic bed. The ideal temperature value would be just above the dew point of the surrogate used as reagent. The bubble and dew points for the surrogate mixtures used in this work are calculated using the following equations:

> Antoine's law

$$\log_{10}P^0 = A - \frac{B}{C+T}$$

A, B, C = Antoine's coefficients

 P^0 = Vapour pressure for pure component (mBar)

 $T = temperature (^{\circ}C)$

> Raoult's law

$$P_i = x_i P_i^0$$
$$P_i = y_i P$$

 P_i = partial pressure for the component i

P = total mixture pressure

 P_i^{0} = partial pressure of component i if it was pure

 χ_i = molar fraction in the liquid phase for component i

 y_i = molar fraction in the vapour phase for the component i

Knowing that for dew and bubble points the following restraints are valid, it is easy to calculate the bubble and dew temperature for the mixture by an iterative calculation:

$$\frac{\sum x_i P_i}{P_{tot}} = 1$$
$$\frac{\sum y_i P_{tot}}{P_i^0} = 1$$

In the following tables (Tables 2-6) are listed the composition and the Antoine's coefficients of the surrogate mixtures.

KEROSENE SURR.	% VOL	А	В	С
Methyl-cyclohexane	14.0	7.00107	1375.13	232.819
Dodecane	65.0	7.22883	1807.47	199.381
T-butylbenzene	10.0	6.88707	1509.57	207.654
Tetralin	5.0	7.16735	1806.14	213.732
Decalin (cis+trans)	6.0	6.82445	1503.12	207.901

Table 2 - Composition of the kerosene surrogate mixture

Table 3 - Composition of the diesel surrogate mixture A

DIESEL SURR. A	% VOL	A	В	С
N-hexadecane	24.0	7.36235	2094.08	180.407
Iso-octane	19.0	6.99021	1358.75	232.214
N-butylcyclohexane	27.0	6.87773	1570.94	212.057
N-butylbenzene	23.0	7.18472	1720.37	216.413
1-Methylnaphtalene	7.0	7.26987	2027.90	217.356

DIESEL SURR. B	% VOL	Α	В	С
N-hexadecane	24.0	7.00107	1375.13	232.819
Iso-octane	19.0	7.22883	1807.47	199.381
N-butylcyclohexane	27.0	6.88707	1509.57	207.654
N-butylbenzene	23.0	7.26987	2027.90	217.356
Tetralin	7.0	7.16735	1806.14	213.732

Table 4 - Composition of the diesel surrogate mixture B

Table 5 - Composition of the gasoline surrogate mixture A

GASOLINE SURR. A	% VOL	Α	В	С
N-heptane	13.5	7.04605	1341.89	223.733
Iso-octane	37.5	6.99021	1358.75	232.214
Cyclo-hexane	9.0	7.00854	1296.23	233.309
Cyclo-hexene	6.0	7.02290	1300.39	230.976
Toluene	30.5	7.13620	1457.29	231.827
Ethanol	3.5	8.13484	1662.48	238.131

Table 6 - Composition of the gasoline surrogate mixture B

GASOLINE SURR. B	% VOL	Α	В	С
N-heptane	15.0	7.04605	1341.89	223.733
Iso-octane	38.0	6.99021	1358.75	232.214
Cyclo-hexane	10.0	7.00854	1296.23	233.309
Cyclo-hexene	7.0	7.02290	1300.39	230.976
Toluene	31.0	7.13620	1457.29	231.827

The temperature of the dew and bubble point at 0.1 MPa pressure (atmospheric pressure is considered the zero so for 0.1 MPa is intended 0.1 MPa over ambient pressure), are reported in Table 7.

Table	7 -	Dew	and	bubble	point	values	for	the	fuel	surrogates
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SURROGATE	DEW POINT (°C)	BUBBLE POINT (°C)
Kerosene	229.8	186.5
Diesel A	256.3	181.9
Diesel B	252.5	181.1
Gasoline A	124.8	120.1
Gasoline B	126.6	123.7

3.2 Activity of ALUSUC2[PtSn] in the partial dehydrogenation of diesel and gasoline

3.2.1 Partial dehydrogenation of the kerosene surrogate

The results of the catalytic PDh test carried out at 450 °C, 1 MPa, $\tau = 2s$ on the kerosene surrogate can be compared to those obtained with LSK and are reported in Fig. 1.



Figure 1 - Hydrogen productivity comparison between LSK and the surrogate mixture

The hydrogen productivity for LSK and the surrogate feedstock are similar, confirming the representativeness of the surrogate mixture. The activity and stability for LSK are slightly lower than that of the surrogate mixture, probably due to the presence of additives and some traces of sulfur containing compounds in LSK. Those also affect the hydrogen purity (measured at 6 hours of reaction) that is 99.3 % vol. using the kerosene

surrogate and decreases to 97.6 % vol. using LSK. Overall it is possible to asses that the surrogate mixture chosen is a good model for LSK.

In Fig. 2 are reported the conversion and selectivity values registered for the reaction with kerosene surrogate.



Figure 2 - Conversion and selectivity for the PDh reaction on kerosene surrogate

From the conversion values it is possible to deduce that the hydrogen produced comes from the aromatisation of the cyclic and dicyclic hydrocarbons, while linear and aromatic ones are not modified by the reaction. Me-cyclohexane, representative of the cyclic compounds, gives toluene with a selectivity close to 100%. Tetralin and decalin, representative of the dicyclic compounds, are almost entirely converted and give the formation of naphthalene with a selectivity of 100%. Those results are very similar to those of kerosene Jet A-1 (discussed in chapter 2.4.6) where the same behaviour was observed: the cyclic hydrocarbons were converted to aromatic and hydrogen while the other classes remain almost unconverted.

3.2.2 Study of the partial dehydrogenation of gasoline

> Gasoline surrogate A - Pressure screening

The dehydrogenation reaction is thermodynamically favoured at lower pressure values, but in heterogeneous catalytic reaction some of the mass transport kinetic, related to the pressure (mass transfer between the vapour and the interface of the catalyst, mass transfer from outside to inside the pores of the catalyst, adsorption-desorption of molecules on the active phase), could be a limiting factor for the hydrogen production.

Therefore two tests at 0.1 MPa and 1 MPa have been performed in order to analyse the difference in hydrogen productivity. In Fig. 3 is shown the pressure screening carried out on gasoline surrogate A. The operational conditions are 350 °C, $\tau = 2s$ and no hydrogen recycling.



Figure 3 - Hydrogen productivity for gasoline surrogate A at different P values

The PDh reaction on gasoline surrogate A seems to be more efficient at 0.1 MPa with a relatively higher activity. Overall the hydrogen productivity is very low for both pressures, with an average of 800 NL·h⁻¹·kg_{cat}⁻¹ at 0.1 MPa

and 500 NL·h⁻¹·kg_{cat}⁻¹ at 10 MPa. The level of production is much lower than the values observed for PDh of kerosene and is not very encouraging.



The hydrogen purity for the two reactions, obtained by GC analysis, is shown in Fig. 4.

Figure 4 - Hydrogen purity at different pressure for gasoline surrogate A

The hydrogen purity is not affected by the pressure change, with almost the same values for the two catalytic tests but a purity of ≈ 70 % vol. is not sufficient to feed PEM fuel-cell without purification. The amount of methane in the outflow is similar to that observed with kerosene (values around 1-2 % vol.), but in the case of gasoline surrogate A the main impurities are ethane, ethene (≈ 20 % vol.) and heavier hydrocarbons (≈ 15 % vol.). The conversion for each component of the surrogate after the two reactions are reported in Fig. 5.





In contrast to what was observed for the kerosene surrogate reaction, the hydrogen production measured for the gasoline surrogate A seems to be derived from cracking reaction of cyclo-hexene. The iso-octane remains unconverted in both cases. The apparent negative conversion of cyclo-hexane results in part from the hydrogenation of cyclo-hexene to cyclo-hexane and, as expected, with increasing pressure the amount of cyclo-hexene that is hydrogenated also increases. The rest of converted cyclo-hexene probably undergoes catalytic cracking reactions resulting in hydrogen and C_2 - C_5 impurities. The toluene is converted to n-heptane via hydrogenation and ringopening. This reaction is undesired because it consumes part of the hydrogen produced. The conversion of ethanol is very high (90 %) and the mechanism proposed is the dehydration of ethanol to form ethene and water. This reaction is reported to take place on the acid sites of alumina or other oxides, as described by Zotov et al., Bedia et al. and Zaki et al. [3-6]. Such a high conversion of the ethanol is though unexpected. This seems to be proportional to the C_2 impurities measured in the outflow, supporting this hypothesis and giving a possible explanation to the scarce hydrogen productivity with the gasoline surrogate A. The ethylene formed can polymerise on the active sites and form a branched precursor of carbon coke, impeding the dehydrogenation reaction. Further studies on the reactivity of ethanol with the ALUSUC2[PtSn] catalyst should be carried out in order to have a better comprehension of this mechanism.

The reaction of partial dehydrogenation on new generation gasoline, that contain large amounts of ethanol, is not convenient for the application desired. Therefore in order to continue the investigation a second surrogate of gasoline, that doesn't contain ethanol, will be used in the next part.

Gasoline surrogate B - Pressure screening

A second gasoline surrogate, that do not containing ethanol, has been tested in this preliminary study. As a pressure of 1 MPa seemed too elevated for the previous screening the values chosen for the next tests are 0.1 MPa and 0.3 MPa. The hydrogen productivity for the pressure screening carried out on the gasoline surrogate B at 400 °C, $\tau = 2s$ and no hydrogen recycle is shown in Fig. 6.



Figure 6 - Hydrogen productivity for gasoline surrogate B at different P values

The tests carried out on the gasoline surrogate B show a considerably higher hydrogen productivity with respect to the tests on surrogate A, with an average of 2000 NL·h⁻¹·kg_{cat}⁻¹ at 0,1 MPa and slightly lower at 0,3 MPa, meaning an enhancement of almost 1500 NL·h⁻¹·kg_{cat}⁻¹. Those results confirm the negative effect of ethanol presence for the PDh reaction with Pt-Sn/ γ -Al₂O₃ catalysts.

The hydrogen purity for the two reactions, obtained by GC analysis, is shown in Fig. 7.



Figure 7 - Hydrogen purity at different pressure for gasoline surrogate B

The hydrogen purity is very similar for both pressures with values that exceed 99 % vol. The main impurity is methane with a value of 0.5 % vol. at 0.1 MPa and 0.3 % vol. at 0.3 MPa. The other impurities of heavier hydrocarbons are present in traces. There is an important difference in hydrogen purity between surrogate A and B passing from \approx 70 % vol. to above 99 % vol. respectively. This effect is due to the absence of ethanol: its dehydration leads to the formation of C₂ impurities in the out-gas up to 20 % vol., causing the decrease of H₂ purity. The hydrogen purity registered for the gasoline surrogate B would definitely allow to feed the produced hydrogen directly to PEM fuel-cells without further purification.

The conversion and selectivity for the two reactions are shown in Fig. 8 and Fig. 9.



Figure 8 - Conversions at different pressure values for gasoline surrogate B



Figure 9 - Selectivity at different pressure values for gasoline surrogate B

The conversion for the surrogate B is more similar to that of the reaction with kerosene. The pressure change doesn't affect the conversion that is almost identical for 0.1 MPa and 0.3 MPa. The conversion of the cyclic hydrocarbons cyclo-hexane and cyclo-hexene, that produce the majority of the hydrogen, is almost 100 %. Those are aromatised to benzene with a selectivity of 100 %. The conversion of the linear hydrocarbons n-heptane and iso-octane also gives a contribution to the hydrogen produced. One possible mechanism of this dehydrogenation route is represented in Fig. 10.



Figure 10 - Mechanism of reaction for n-heptane and iso-octane conversion to toluene

The selectivity to toluene decreases with the increasing of the pressure passing from a value of \approx 90 % to \approx 60 %. The n-heptane and iso-octane that are not converted to toluene undergoes probably catalytic cracking or lead to the formation of olefin followed by formation of coke precursors. Unexpectedly the diminution of the selectivity to toluene is not accompanied by an increase of CH₄ impurities related to an increase in cracking reaction.

Gasoline surrogate B - Temperature screening

The hydrogen productivity for different temperatures obtained with gasoline surrogate B at 0.1 MPa, $\tau = 2s$ and without hydrogen recycling are shown in Fig. 11:



The hydrogen productivities at 450 °C and 400 °C are comparable, with an average production of $\approx 2000 \text{ NL} \cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$. When the temperature is lowered to 350 °C a loss in productivity is observed, leading to an average of $\approx 1600 \text{ NL} \cdot \text{h}^{-1} \cdot \text{kg}_{cat}^{-1}$. Therefore the temperatures of 400 °C and 450 °C corresponds to the maximum in the hydrogen productivity for the PDh.

In Fig. 12 are reported the hydrogen purity values for the reactions at different temperatures.



Figure 12 - Hydrogen purity at different temperature values for gasoline surrogate B

Hydrogen purity at 350 °C and 400 °C is exceeding 99 % vol., while a diminution to 97.5 % vol. is measured when the temperature is increased 450 °C. At 450 °C the cracking reactions start to be favoured, leading to an increase of CH_4 and other light hydrocarbons impurities. Catalytic cracking is a very well known reaction that is catalysed by acid sites. Depending on the strength of the acid sites and the type of hydrocarbon, the catalytic cracking usually takes place at temperature higher than 400 °C [7–9] and contributes to the formation of coke precursors that cause the catalyst deactivation. Therefore the best temperature for the PDh of gasoline surrogate B, is 400 °C at which the ratio between dehydrogenation/cracking is maximised with the ALUSUC2[PtSn] catalyst.

The compounds that display the higher conversion (Fig. 13) are the cyclic hydrocarbons, which are the major hydrogen source for the PDh reaction. At 350 °C the conversion of cyclo-hexane is not complete explaining
the lower hydrogen productivity at 350 °C compared to 400 °C and 450 °C. The conversions of the linear hydrocarbons increase with the temperature but the values are relatively low with a maximum of 12 % for the n-heptane at 450 °C. As previously explained the toluene conversion is negative because it is formed by dehydrocyclisation of n-heptane and iso-octane.



Figure 13 - Conversions at different temperature values for gasoline surrogate B

As shown in Fig. 14, the selectivity to toluene decreases when the temperature increases because the reaction of catalytic cracking become favoured. The selectivity for the dehydrogenation of cyclo-hexane and cyclo-hexene to benzene is 100 % for all the temperatures.





Gasoline surrogate B - Study of the effect of the hydrogen recycle

In order to improve the catalyst stability, the effect of the introduction of hydrogen recycling has been studied. The use of hydrogen recycling to increase catalyst stability is a common procedure in many industrial processes for reaction as reforming or dehydrogenation. The effect is to decrease the deactivation via carbon coke deposition. In this part of the study on gasoline surrogate B a catalytic test at 400 °C, 0.1 MPa $\tau = 2s$ and 7 % vol. hydrogen recycling has been performed. This result is compared to a test conducted in the same conditions, but without the hydrogen recycling.

In order to have a more reliable extrapolation for the estimation of the catalyst lifetime, those catalytic tests are performed for a duration of 6 hours. Fig. 15 presents the hydrogen productivities with and without the hydrogen recycling:



Figure 15 - Hydrogen productivity with and without hydrogen recycle for gasoline surrogate B

When the hydrogen recycling is introduced, a slight decrease in productivity is noticed as the equilibrium of the dehydrogenation reaction is moved towards the reagents. This small loss of productivity is accompanied by a considerable increase of the stability: the lifetime, increase from 118 hours in absence of recycle to 376 hours with the recycle. Those lifetimes are higher with respect to the results obtained with the kerosene surrogate and are very promising for concrete application if confirmed for real gasoline fuel PDh. The hydrogen purity for the two reactions are reported in Fig. 16.



Figure 16 - Hydrogen purity as function of hydrogen recycle simulation for gasoline surrogate B

The hydrogen produced is almost pure, exceeding in both cases 99 % vol. The main impurity is methane which increases from a value of 0.2 % to 0.6 % when the hydrogen recycling is introduced. The higher hydrogen partial pressure in the reaction atmosphere, besides shifting the equilibrium, also favours the hydrocracking reaction, leading to a slight increase in CH_4 formation. The purity decrease is very limited compared to the gain in terms of stability; therefore it is preferable to work with a 7 % vol. hydrogen recycle in the feed. The conversion and selectivity for the two reactions, reported in Fig. 17 and Fig. 18, show that the introduction of the recycle doesn't affect the reactivity of the surrogate mixture.



Figure 17 - Conversions as function of hydrogen recycle for gasoline surrogate B



Figure 18 - Selectivity as function of hydrogen recycle for gasoline surrogate B

The best parameters identified for the PDh of gasoline surrogate B are 400 °C, 0,1 MPa, $\tau = 2s$, 7 % H₂ recycle allowing a 1750 NL·h⁻¹·kg_{cat}⁻¹ average production of 99 % vol. pure hydrogen for a catalyst lifetime of more than 350 hours.

> Comparison between the gasoline surrogates reactivity

The behaviours of the two gasoline surrogates are very different. The presence of ethanol is a key parameter for the activity in terms of hydrogen production. The comparison between gasoline surrogates A and B, in terms of hydrogen production and carbon coke formation analysed by TGA/DTA is shown in Fig. 19.



Figure 19 - Comparison between gasoline surrogates A and B: productivity and coke deposition

The hydrogen productivity for the surrogate A, containing ethanol, is considerably lower than for surrogate B and the purity is also affected with a 70 % vol. for the surrogate A against the 99 % vol. for the surrogate B. The ethene formed via ethanol dehydration lead to a faster deactivation of the catalyst by coke deposition. The carbon formed is very different for the two surrogates: the carbon formed with surrogate B is less than the amount formed on surrogate A and for the latter a prominent peak at low temperature (225 °C) could be attributed to a disordered type of carbon formed nearby the active phase, probably caused by the polymerisation of the ethylene formed.

3.2.3 Study of the partial dehydrogenation of diesel

> Diesel surrogate A - Temperature screening

The partial dehydrogenation reaction has been carried out on the diesel surrogate A at two different temperatures (350°C, 450°C) in order to have a first evaluation of the reactivity. The hydrogen productivity obtained for the two catalytic tests carried at 0.1 MPa, $\tau = 2s$ without hydrogen recycling are shown in Fig. 20.



Figure 20 - Hydrogen productivity plots at different temperatures for diesel surrogate A

The hydrogen production using diesel surrogate A is very low for both temperatures and the deactivation is the fasted that has been observed among the different reagent tested with the ALUSUC2[PtSn] catalyst. The amount of hydrogen produced and the lifetime of the catalyst are far from any possible practical application using a fuel approaching this surrogate composition.



Figure 21 - Hydrogen purity at different temperatures for diesel surrogate A

As also observed for kerosene and gasoline, the hydrogen purity (Fig. 21) decreases when the reaction temperature is raised because of the cracking reactions increasing. The purity values are around 96 % vol. and should still allow to directly feed PEM fuel-cell. A study on how much the presence of CH_4 impurity affects the fuel-cell efficiency should be considered in this case.



Figure 22 - Conversions at different temperatures for diesel surrogate A

The conversion (Fig. 22) is very low for all the compounds present in the surrogate at both temperatures (explaining the low hydrogen production) and the catalyst deactivation is very fast. The carbon coke deposited on the catalyst have been analysed by TGA/DTA analysis; the results are shown in Fig. 23.



Figure 23 - TGA/DTA analysis performed on the spent catalyst after reaction on diesel surrogate A

The amount of carbon coke formed during 4 hours of reaction is very high compared to the values observed with gasoline surrogates and kerosene, with a value of 8.2 % wt. at 350 °C and 13.1 % wt at 450 °C. Such high amounts of carbon coke deposited are registered for industrial reforming catalysts after a TOS of the magnitude of months, as highlighted by the works of He et al. and Baghalha et al. [10,11]. This high amount of coke deposited has been attributed to the presence of 1-methylnaphtalene in the surrogate. As also observed by Blancharde et al. and Kabe et al. [12,13], methylnaphthalene can form a radical, leading to the formation of polyaromatics via polycondensation and consequently to the formation of coke. The mechanism proposed is illustrated in Fig. 24:



Figure 24 - Carbon coke formation mechanism from 1-methylnaphtalene

> Diesel surrogate B - Temperature screening

In order to better understand this phenomenon and to validate this hypothesis another study has been performed using a second diesel surrogate. The diesel surrogate B contains tetralin as representative for the bi-cyclic class instead 1-methylnaphtalene.

The partial dehydrogenation of diesel surrogate B have been carried out a three different temperatures (350 °C, 400 °C, 450 °C) and at 0.1 MPa, $\tau = 2s$ without hydrogen recycling. The results of this temperature screening are shown in Fig. 25:



Figure 25 - Hydrogen productivity plots at different temperatures for diesel surrogate B

The hydrogen production obtained with the diesel surrogate B is more than 10 times higher than for diesel surrogate A, confirming that the low activity obtained was caused by the presence of 1-methylnaphtalene in the surrogate mixture. The more important difference is noticed between 350 °C to 400 °C with an increase of the productivity from an average of 2000 NL·h⁻¹·kg_{cat}⁻¹ to 3750 NL·h⁻¹·kg_{cat}⁻¹. At a temperature of 450 °C an additional, but less considerable increase in productivity is registered. The hydrogen purity measured at the end of the reaction for the three temperatures is shown in Fig. 26.





Hydrogen purity is extremely high at 350 °C and 400 °C with values very close to 100 % vol. while at 450 °C the cracking reaction cause an increase of the methane impurity to over 2 % with a consequent decrease of the hydrogen purity. The best compromise between hydrogen production and purity is achieved at 400 °C, that is chosen as optimal temperature for the PDh of diesel surrogate B.



Figure 27 - Conversions at different temperatures for diesel surrogate B

The conversion for the components of the diesel surrogate B (Fig. 27) reflects what was already observed for kerosene and gasoline fuels, with the cyclic hydrocarbons displaying an elevated reactivity and the paraffins remaining unreactive.

The noticeable gap in productivity between 350 °C and the other temperatures is related to the n-butylcyclohexane conversion that, together with the tetralin, is the principal source of hydrogen for this reaction. At 350 °C the conversion of butyl-cyclohexane is still very low (≈ 25 % vol.) and increases prominently at 400 °C and 450 °C to 75 % vol. and 80 % vol. respectively. Tetralin is the most reactive component of the surrogate mixture with a conversion of almost 100 % vol. for all the temperatures tested. As shown in Fig. 26 the conversion of tetralin to naphthalene takes place with a selectivity of 100 % independently from the temperature. The conversion of

butyl-cyclohexane to butyl-benzene reaches 100 % selectivity only at 400 °C and 450°, while at 350 °C the selectivity is slightly lower (Fig. 28).



Figure 28 - Selectivity at different temperatures for diesel surrogate B

> Diesel surrogate B - Pressure screening

In order to confirm the trend observed with the other surrogates, two tests at different pressure (0.1 MPa, 0.3 MPa) have been performed on diesel surrogate B at 400 °C, $\tau = 2$ s without hydrogen recycling. The hydrogen productivity registered are shown in Fig. 29.



As for the previous results, a diminution in terms of hydrogen production is observed with increasing pressure, suggesting 0.1 MPa as the best pressure for the PDh of diesel surrogate B. As shown in Fig. 30, the hydrogen purity is not affected by the increase of pressure from 0.1 MPa to 0.3 MPa.



Figure 30 - Hydrogen purity at different temperatures for diesel surrogate B

The conversion and selectivity as function of the pressure are shown in Fig. 31 and Fig. 32 respectively:



Figure 31 - Conversions at different pressures for diesel surrogate B



Figure 32 - Selectivity at different pressures for diesel surrogate B

The proportion between the conversion for each component for the two pressure values is retained, but at 0.3 MPa a slight diminution of the conversion is observed for each component. The selectivity remains 100 % regardless the pressure.

> Diesel surrogate B - Study of the effect of the hydrogen recycling

In order to improve the catalyst stability, the effect of the introduction of hydrogen recycling has been studied. Two catalytic tests on diesel surrogate B have been performed at 400 °C, 0.1 MPa and $\tau = 2s$ with and without the introduction of a 7 % vol. hydrogen. The hydrogen productivity for the 6 hours catalytic tests is shown in Fig. 33.



Figure 33 - Hydrogen productivity plots with and without hydrogen recycle for diesel surrogate B

The hydrogen production slightly decreases with the hydrogen recycling as the reaction equilibrium is shifted towards the reagents, but an increase in catalyst stability is noticed. The lifetime increase is not as pronounced as observed for gasoline surrogate B, but the hydrogen productivity with the diesel surrogate is considerably higher, with a productivity as high as 3000 NL·h⁻¹·kg_{cat}⁻¹ for the 6 hours of reaction. The hydrogen purity (Fig. 34) is very similar for the two tests with values that exceed 99 % vol. Only a 0.1 % vol. increase in the +C₂ impurities is noticed, due to an increase of the hydrocracking reaction.





The conversion and selectivity for the catalytic reactions, reported in Fig. 35 and Fig. 36 respectively, show no difference between the test with and without hydrogen. It is noticed though that while the n-butylcyclohexane conversion to n-butylbenzene had 100 % selectivity for the 4 hours reaction, this value is now decreased at 89 % for the 6 hours reaction.



Figure 35 - Conversions as function of hydrogen recycle for diesel surrogate B





> Comparison between the diesel surrogates reactivity

For the diesel surrogates the presence of 1-methylnaphtalene in the mixture is the factor that limits the feasibility of the process. In Fig. 37 is shown the comparison between diesel surrogates A and B, in terms of hydrogen production and carbon coke formation analysed by TGA/DTA:



Figure 37 - Comparison between diesel surrogates A and B: productivity and coke deposition

The hydrogen productivity for the surrogate A, which contains 1methylnaphalene as representative of the naphthene class, is more than 10 times lower than for surrogate B, which contains tetralin as representative of the naphthene class. The purity is also affected: for the surrogate A the purity is under 96 % vol. while for surrogate B it is over 99 % vol. The 1methylnapthalene leads to an immediate and rapid deactivation of the catalyst by coke deposition by the mechanism explained in the previous chapter (3.3.3). The high amount and the nature of the coke formed during reaction are responsible of the fast deactivation observed with surrogate A. The huge peak at 450 °C can be attributed to a highly ordered type of carbon formed by polycondensation of the radicals derived from methylnaphalene. This peak is in fact absent in the case of surrogate B where tetralin is used instead.

3.2.4 Fuel surrogates reactivity comparison

The PDh reaction of gasoline and diesel applied to high purity hydrogen delivery finalised to feed PEM fuel-cells is a promising option. In the case of gasoline this application must be limited to ethanol free gasoline. In the case of diesel the applicability of this concept depends on the types of naphthene contained in the fraction, as it has been observed that certain compounds like 1-methylnaphtalene can cause the immediate deactivation of the catalyst.

The comparison in terms of hydrogen productivity between kerosene, gasoline and diesel surrogates at the optimal operational conditions is shown in Fig. 38.



Figure 38 - Fuel surrogates PDh comparison

Kerosene and diesel surrogates show the best values of hydrogen production with an initial value of $\approx 3800 \text{ NL}\cdot\text{h}^{-1}\cdot\text{kg}_{cat}^{-1}$. The lifetime extrapolated from the curve is lower for diesel surrogate: 39 hours against the 156 hours for kerosene surrogate. This difference can be attributed to a couple of factors: higher linear hydrocarbons conversion in diesel surrogate, which can form coke precursors and leads to catalyst deactivation and the nature of cyclic hydrocarbons contained in the two surrogate mixtures. In kerosene surrogate the representative molecule for cyclic hydrocarbons is methylcyclohexane that is converted to toluene with a 100 % selectivity, while in diesel surrogate the representative molecule is n-butylcyclohexane which converts to n-butylbenzene with an 86 % selectivity. Part of the nbutylcyclohexane converted is transformed to coke via undesired reactions like cracking, condensation or polymerisation. This would explain the different stability between kerosene and diesel surrogates. Gasoline surrogate display a lower hydrogen productivity with an average value of 1800 NL·h⁻ ¹·kg_{cat}⁻¹, on the other hand the catalyst stability is more than doubled with respect to kerosene surrogate with a lifetime of 376 hours. In this case the conversion of linear hydrocarbons contributes more to the hydrogen and affects the deactivation production less according the to dehydrocyclisation mechanism explained in chapter 3.3.2.

The reactivity of each class of compound is different for the three surrogates, but mainly the hydrogen generated is produced by dehydrogenation of cyclic and bi-cyclic hydrocarbons, with a little contribution from the linear paraffins. The contribution to the hydrogen produced by each class of compound for the three surrogates is schematised in Fig. 39. The hydrogen production is expressed in normal litres of hydrogen for minutes, supposing to use a reactor with one kg of catalyst.





Partial dehydrogenation of fossil fuels finalised to high purity hydrogen generation for PEM fuel cells is an interesting option to achieve better efficiency in on-board electricity generation. The applicability of this concept to diesel and gasoline seems feasible after the analysis of the results of this preliminary study. The reactivity depends on the fuel composition and it has been proved that gasoline must be ethanol free and that for diesel PDh the presence of methyl substituted naphthalenes has a deleterious effect. The trend observed seems to be that for heavier hydrocarbons hydrogen produced is increased but the catalyst stability decreases. The hydrogen purity is in all cases over 99 % vol. which allows to directly feed PEM-FC.

The subsequent step to continue the study and validate these results would be to test the PDh of commercial diesel and gasoline fuels.

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4. Conclusions

The development of more electrified and environmentally friendly means of transport, in order to significantly reduce greenhouse gases emissions, can be achieved with the implementation of fuel-cell power unit on-board vehicles. However, for this purpose, the implementation of an hydrogen supply must be developed. The most known processes for hydrogen production, like reforming or partial oxidation of hydrocarbons, present various inconveniences for the on-board applications. Therefore, in this work, the feasibility of the catalytic partial dehydrogenation (PDh) process for the direct on-board hydrogen generation, finalised to the alimentation of a fuelcells based auxiliary power system, has been investigated.

The partial dehydrogenation of kerosene was studied for on-board applications on airplanes and the studies on the PDh of gasoline and diesel were performed with the purpose of extending this technology to other vehicles.

The choice of the catalyst is crucial for the partial dehydrogenation process; it must produce H_2 without compromising the original fuel properties. An ideal catalyst must be sulfur tolerant, generate sufficient hydrogen of high purity, be selective to dehydrogenation and avoid cracking reactions responsible for coke deposition and catalyst deactivation. This study on the partial dehydrogenation of kerosene highlighted that the porosity of the catalytic material is a key aspect for the activity and stability. Very small pores, close to micropore region, are more easily plugged by carbon deposition, while mesoporous materials with high pore volume seems to be the ideal candidate for fuels PDh reaction. The acidity of the materials is another important factor for the catalytic properties. From what has been observed, the prevalence of strong acid sites is deleterious for the PDh reaction as those can catalyse cracking reactions that lead to the formation of coke precursors. The presence of mild acid sites can help increasing the hydrogen productivity catalysing isomerisation and cyclization reactions. A good value of acidity is in the range of 100-200 μ mol_{NH3}·g⁻¹. As a consequence γ -Al₂O₃ results to be a very good compromise between the costs, activity and ease of synthesis.

In this thesis work, two materials have been highlighted as the best catalysts for the partial dehydrogenation of kerosene: a trimetallic 1%Pt-1%Sn-0.5%In/ γ -Al₂O₃ (Cat-In[0.5]) supported on a commercial alumina and a bimetallic 1%Pt-1%Sn/y-Al₂O₃ (ALUSUC2[PtSn]) supported on a new sucrose templated alumina. Those catalysts have been used in the partial dehydrogenation of kerosene working at the optimised operating conditions of 450 °C, 1 MPa, $\tau = 2$ s and 7 % H₂ recycling. The results for ALUSUC2[PtSn] shows an average hydrogen production of 3500 NL \cdot h⁻¹ \cdot kg_{cat}⁻¹ with a purity of 97.6 % vol. and a lifetime of 79 h. With the catalyst Cat-In[0.5] an average hydrogen production of 2900 NL \cdot h⁻¹·kg_{cat}⁻¹ with a purity of 97.8 % vol. and a lifetime of 107 are obtained. The hydrogen purity is similar in both cases, but trimetallic Pt-Sn-In/y-Al₂O₃ show a different reactivity leading to an improvement of the lifetime. The low ratio between strong and weak acid sites is effective in reducing undesired side reactions such as cracking. As a consequence, the carbon coke formation is decreased and the catalyst activity is maintained for longer time. More specifically, we have shown that the presence of indium reduces the amount of coke formed in the proximity of Pt particles. The higher hydrogen production obtained with ALUSUC2[PtSn] is related to the use, as support, of a sucrose templated alumina, which shows an enhancement in the specific surface area and pore volume compared to the commercial alumina used for Cat-In[0.5].

The fractionation of kerosene by distillation, allows creating of fractions enriched in the desired type of hydrocarbons (cyclic, naphtenes). This also leads to a considerable decrease of the sulfur content with respect to the original Jet A-1, which allows to further increase the activity and stability of the catalyst. The hydrogen productivity obtained with the partial dehydrogenation of 5-14 % wt. fractions is increased of almost three times with respect to the reaction carried out on Jet A-1. The investigation on PDh of kerosene in the "GreenAir" project was required to achieve various technical milestones. Those milestones are reported in Table 1 and put in perspective with the results of Cat-In[0.5] and ALUSUC2[PtSn].

PARAMETERS	TARGET	ALUSUC2[PtSn]	Cat-In[0.5]
H ₂ production (NL·h ⁻¹ ·kg _{cat} ⁻¹)	1000	3500	2900
Electric Power (kWe)	1	3.5	2.9
Lifetime (h)	100	79	107
H ₂ purity (% vol.)	> 95	97.6	97.8
Sulfur tolerance (ppmw)	300	3	3
Start-up time (min)	< 15	≈ 30	≈ 30

Table 1 - Evaluation of the results in the partial dehydrogenation of kerosene for the "GreenAir" project

¹Depends on the efficiency of the heat recovery from other sources for kerosene evaporation

The hydrogen productivity, the hydrogen purity and the catalyst lifetime achieved are sufficient to fulfil the target previewed. The start-up time of the laboratory scale test rig is around 30 min and is due to the stabilisation of the heater's temperature and system pressurization; in a pilot reactor with more efficient heater and pressure control the start-up time can be easily reduced to less than 15 min. The results obtained showed that the catalytic partial dehydrogenation of kerosene is a promising technology for the direct on-board production of high purity hydrogen.

The partial dehydrogenation of ethanol free gasoline (surrogate B), performed using ALUSUC2[PtSn] at 400 °C shows an average hydrogen production of 1800 NL·h⁻¹·kg_{cat}⁻¹ with a purity of over 99 % vol. and a lifetime of 376 h. The study highlighted that the catalytic material is very sensitive to the presence of ethanol in the mixture. The tests performed on a gasoline containing 3.5 % vol. of EtOH (surrogate A), show a very fast deactivation

due to the dehydration of ethanol to ethene, which via polymerisation forms coke precursors and causes the deactivation of the catalyst.

The partial dehydrogenation of a surrogate representative of diesel (surrogate B: 24% N-hexadecane, 19% Iso-octane, 27% Butyl-cyclohexane, 23% Butyl-benzene, 7% Tetralin), with the catalyst ALUSUC2[PtSn], performed at 400 °C shows an average hydrogen production of 3500 NL·h⁻¹·kg_{cat}⁻¹, a purity of over 99 % vol. and a lifetime of 29 h. The study highlighted that the catalyst is strongly affected by the presence of a specific type of naphtene in the mixture. The tests performed on a diesel containing 7 % vol. of 1-methyl-naphthalene (surrogate A: 24% N-hexadecane, 19% Iso-octane, 27% Butyl-cyclohexane, 23% Butyl-benzene, 7% 1-Methyl-naphthalene), displayed a very fast deactivation due to the formation of a bicyclic radical that via polycondensation forms a graphitic type of carbon.

The reactivity of the different surrogates changes with the hydrocarbons composition. The behaviour suggests that the catalyst stability is inversely proportional to the carbon chain length distribution of the fuel, while the hydrogen productivity increases with it. Considering having a reactor with 1 kg of catalyst, the total production is similar for kerosene and diesel surrogates with a value close to 5.4 NL·min⁻¹ and lower for the gasoline surrogate with a value close to 3 NL·min⁻¹ (Fig. 1). The common point is that the majority of the hydrogen produced comes from the dehydrogenation of cyclic molecules that are more reactive. Cyclic and bi-cyclic hydrocarbons are dehydrogenated to the corresponding aromatic or napthene showing high conversions (80-100 %) and selectivity (100 %). The linear molecules, in the case of kerosene and diesel surrogates, give a very small contribution and show very low conversions. Exception is made for the gasoline surrogate where the shorter linear hydrocarbons (C₇-C₈) contribute more significantly to the hydrogen production following a dehydrocyclization-aromatisation pathway.



Figure 1 - Fuel surrogates hydrogen productivity per class of compound

The partial dehydrogenation of fuels showed high hydrogen productivity with high purity and a relatively low coke deposition on the catalyst. The lifetime of the materials is sufficient in the case of gasoline and kerosene PDh, but it may be further improved. However the results of this study allow assessing that the partial dehydrogenation of fuels is convenient method for the on-board hydrogen generation finalised to the alimentation of fuel-cell APU, at the condition that they don't contain more than 3 ppm of sulfur.

For future developments, in the direction of using a standard Jet A-1 as feedstock, a new thio-resistent catalyst should be designed for the PDh of sulfur rich fuels, or in alternative, a desulfurisation step need to be added before the PDh reaction. One possibility could be to perform a rectification of the Jet A-1 just before the PDh, in order to increase the activity and stability.

Further improvements of the process and the catalytic materials should be carried out. In particular, with regards to the materials, the modification of ALUSUC2[PtSn] catalyst with indium is one of the first possibilities to consider. In the direction of the process optimisation, ulterior catalytic dehydrogenation tests with bio-fuels and commercial gasoline and diesel need to be performed in order to verify the preliminary results obtained with the surrogate mixtures. As observed for kerosene, the more complex chemical composition of fuels with respect to the surrogates and the presence of additives in the fuels can affect the results of PDh reaction. Annexes

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High purity hydrogen from catalytic partial dehydrogenation of kerosene using saccharide-templated mesoporous alumina supported Pt–Sn



CATALYSK

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1. Introduction

In the last two decades, fuel cells have reached a place in the vanguard of power generation technologies, but the means to a sustainable and economically feasible hydrogen supply must be developed. Many options for hydrogen storage have been proposed, liquid or high pressure hydrogen storage [1], metal hydride storage [2], generation by aluminium hydrolysis [3], adsorption on different supports [4,5] and thermo-chemical cycles [6]. A promising alternative is hydrogen generation following chemical storage and subsequent on-board consumption, because it avoids some of the technical and safety issues associated with molecular hydrogen storage. Hydrogen can be released from a vast number of compounds including ammonia, formic acid, or hydrazine [7,8], but hydrocarbons are attractive due to their cost and availability. Several processes are currently in use for hydrogen production, like thermal and catalytic cracking, water electrolysis, coal and biomass gasification, hydrocarbon reforming and hydrocarbon

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ABSTRACT

Hydrogen is an element of high economic interest, having significant perspectives for future use in applications as an energy vector. Nowadays H₂ is produced mainly from hydrocarbons in large scale steam reforming plants. However, local integrated generation of hydrogen to directly feed PEM fuel cells is emerging as a promising technology, with the advantages of being adaptable to the transport sector and avoiding the problems associated with the storage of gaseous hydrogen. Partial dehydrogenation of transport fuels is attracting increasing interest in this context. Partial dehydrogenation of jet fuel requires the development of specific catalysts, amongst which Pt–Sn supported on a high surface γ -Al₂O₃, shows good activity and selectivity, leading to production of high purity hydrogen. A strong influence of the textural properties of the support and the chloride content on the hydrogen productivity is observed. © 2013 Elsevier B.V. All rights reserved.

> dehydrogenation [9,10]. Transportation fuels, like diesel or kerosene, can be considered a source of stored hydrogen, and this option has been studied as new way to obtain hydrogen in specific scenarios, like on-board generation of hydrogen as fuel cell feedstock for power generation. Different catalytic processes have been proposed [11-16] to derive hydrogen from diesel and kerosene. Partial dehydrogenation (PDh) of hydrocarbon based fuels is attractive because of their availability, and the potential integration of a PDh process with current technologies. Further, the absence of oxygen in kerosene, for example, implies that the hydrogen stream produced will be free of CO, which could therefore be used directly to feed an on-board proton exchange membrane fuel cell, potentially without further purification or treatment. On the other hand, Partial dehydrogenation of kerosene fuel has great potential for implementation in future development of the aircraft electrification [15,16], the hydrogen generated on-board being used in a fuel cell auxiliary power unit, and the partially dehydrogenated product being returned to the fuel tank [15].

> Much has been published about the use of the Pt and Ni as active phases for catalytic systems in reforming and dehydrogenation of hydrocarbons, using many types of supports [13,15–19]. In these cases, the use of mild conditions produces less cracking on the hydrocarbon molecules, one of the main pathways for coke

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formation. The formation of Pt–Sn alloy phases supported over alumina has been reported as being active for dehydrogenation reactions, and also for the PDh of hydrocarbon mixtures [15] and ultra low sulfur kerosene (ULSK) [16].

We describe below the development and characterization of novel porous alumina supports for Pt–Sn by using glucose and sucrose as templates and AlCl₃ as aluminium source, and the catalytic performance in partial dehydrogenation of ULSK.

2. Experimental

2.1. Catalyst preparation

The method used for support synthesis was based on the work of Xu et al. [20]. In this work, AlCl3·6H2O was dissolved in water, and glucose or sucrose was added with a molar ratio Al:sugar:H₂O 1:1:75. Afterwards, a solution of NH₃ (30 wt%) was added dropwise to adjust the pH to 5 while stirring at 500 rpm. Sucrose, glucose and aluminium chloride were purchased from Sigma-Aldrich. After stirring for 5 h, the resulting gel was heated at 80 °C until dry and calcined at 550 °C for 6 h, using a ramp rate of 2 °C min⁻¹. The active phase was added to the support by incipient wetness impregnation using a solution of H2PtCl6·xH2O(Alfa Aesar) and SnCl2·2H2O(Acros) as precursors, to give a ratio 1 wt%. Pt and 1 wt% Sn (Pt/Sn=0.61 molar ratio). The tin precursor was dissolved in 1 M HCl and then mixed with the platinum salt solution. The solution turned redorange, due to the formation of Pt-Sn-Cl complexes [21]. After drying the impregnated materials overnight at 80°C, they were thermally treated at 120 °C for 2 h and then at 560 °C for 2 h. These support materials are denoted ALUGLU and ALUSUC respectively, while the suffix PtSn refers to the catalyst as prepared. A reference catalyst was prepared using a commercial alumina (Sasol type SCFa140, labelled JM ref.) and containing the same amount of Pt and Sn and prepared in the same way. Part of the catalyst samples was further steam-treated in a tubular oven (H2O/N2 at 550 °C for 2 h), in order to study the influence of dechlorination on catalyst performance. These dechlorinated catalysts are given the further suffix D (i.e. ALUGLUPtSn D).

2.2. Characterization

Structural investigation of the samples was performed by X-ray diffraction, using a *PANalytical X'Pert* diffractometer, using Cu K α radiation (λ = 0.15418 nm, 40 kV, 25 mA) with an acquisition time of 30 min. Phase identification was performed using *HighScore* software by *PANalytical*.

Adsorption–desorption N₂ isotherms at -196 °C were carried out with an ASAP2020 system from Micromeritics. Samples were outgassed at 200 °C for 8 h under a vacuum of 0.5 mmHg. Specific surface area was calculated using the BET method and the pore size distribution using the BJH method and the ASAP2020 implemented software.

Transmission electron microscopy (TEM) imaging was performed using a *JEOL 1200 EX* II microscope working at 100 kV. Samples were dispersed in ethanol and dropped over Cu grids.

The chemical composition was determined by wavelength dispersion X-ray fluorescence spectroscopy (WD-XRF) using a PANalytical AxiosMax apparatus working at 4 kW. Data analysis and semi-quantitative calculations were performed using the SuperQ software of PANalytical.

The metal dispersion was calculated from H_2 chemisorption isotherms using an ASAP 2010C apparatus. 100 mg of sample were reduced under a H_2 flow for 2 h at 350 °C prior to analysis, and evacuated for a further 2 h. H_2 chemisorption isotherms were obtained by measuring the adsorbed amount of H_2 for pressures varying from 10 to 600 mmHg at 35 °C. After completing the initial analysis, the reversibly adsorbed gas was evacuated and the analysis repeated to determine the chemisorbed molecules only.

The surface acidity of materials was studied by NH₃ temperature-programmed desorption (NH₃-TPD), using an *Autochem 2910* automatic system from *Micromeritics*. Samples were heated to 550 °C in a He flow then cooled to 100 °C. Then a flow of pure NH₃ was passed through the samples for 1 h, which were then flushed with He at 100 °C for 1 h. NH₃ was thermally desorbed up to 600 °C with a heating ramp of 10 °C min⁻¹ and detected using a TC detector.

 H_2 temperature-programmed reduction (H_2 -TPR) was performed in an *Autochem 2910* apparatus. Prior to the analysis, the sample was heated to 550 °C for 30 min. under a 30 ml min⁻¹ flow of He. After cooling to 50 °C, a 30 ml min⁻¹ flow of $H_2(5\%)/N_2$ mixture was flowed over the sample, which was heated at 10 °C min⁻¹ up to 700 °C, recording the H_2 consumption with a TC detector.

In order to determine the amount of carbon deposited on used catalysts, thermogravimetric analyses were performed using a *SETARAM Labsys* TG/DTA/DSC system, working in dynamic-air flux mode. Before the analysis, samples were outgassed overnight to eliminate any residue of volatile products in the samples. The thermal programme (20–700 °C), used a ramp of 5 °C min⁻¹, under a flow of synthetic air of 50 ml min⁻¹.

2.3. Catalytic performance on kerosene PDh

The PDh reaction on ultra low sulfur kerosene (S < 3 ppm), ULSK, was performed in a stainless steel fixed-bed tubular reactor. Before the reaction, the catalyst was reduced at atmospheric pressure with a H₂/Ar flow (4:6, v/v) at 350 °C for 2 h. A vapour flow of ULSK, together with a 7 vol.% of H₂ (to simulate a recycle), was fed with a volumetric pump to the reactor containing pelletized catalyst (*d*=1-0.85 mm) at *T*=450 °C and *P*=10 bar. These flows were regulated in order to obtain a contact time τ = 2 s (calculated at STP). After condensing the dehydrogenated kerosene at room temperature and -20 °C using a double condenser, hydrogen production rate (NI H₂ h⁻¹ kg_{cat}⁻¹) was calculated from measurement of the gas out-flow with a digital mass flow metre (*Brooks 5860S1 Smart II* mass flow metre), and the data processed with *LabView* 8.2 instrumentation software. Hydrogen production rate was calculated using Eq. (1):

$$H_2 \text{ production rate} = \frac{\text{Gas Flow} \times (H_2 \text{ Concentration}/100)}{m_{\text{cat}}}$$
(1)

Hydrogen net productivity is easily calculated by subtracting the recycled amount (7%) from the mass flow metre reading and adjusting the sensitivity factor by comparison with a volumetric flow metre installed downstream. A scheme of the reaction rig is shown in Fig. 1. Hydrogen purity was analysed with a gas chromatograph *Agilent 7890A* with a dual column *HP-PLOT molesieve 5A* with TC to analyse the hydrogen and *HP-PLOT/Q* with FI detector to analyse the light hydrocarbons produced. The performance was compared with as prepared and dechlorinated catalysts.

3. Results and discussion

3.1. Catalyst activity

The hydrogen productivity plots for as-prepared and dechlorinated samples of ALUGLUPtSn and ALUSUCPtSn catalysts are shown in Fig. 2. Different profiles are observed depending on the nature of the support and its residual chlorine content. Data on catalytic performance and the projected time until productivity drops to 1000 NI h⁻¹ are collected in Table 1. The deactivation factor (DF) and the lifetime are calculated on the basis of a linear interpolation Á. Reyes-Carmona et al. / Catalysis Today 210 (2013) 26-32



Fig. 1. Simplified reactor scheme used for PDh of kerosene. MFC, mass flow controller; G/L sep, gas liquid separator; MF, mass flow sensor; GC, gas chromatograph.



Fig. 2. Hydrogen productivity plots. Reaction conditions: $T - 450 \,^{\circ}$ C, $P - 10 \,^{\circ}$ Lar, $\tau - 2 \,^{\circ}$ S. Left: as prepared. Right: after dechlorination treatment.



Fig. 3. Evolution of hydrogen purity versus time. Reaction conditions: T-450°C, P-10 bar, τ -2 s.

of the H_2 productivity data in the range of 120–240 min of time on stream. The lifetime has been calculated from the productivity plots using a linear interpolation, taking the values between 120 and 240 min. The deactivation factor (DF) is the rate of loss of productivity per kg of catalyst, and is derived from the slope of the interpolation line. The value of lifetime to 1000 Nl h⁻¹ is taken directly from the plot.

Regardless of use of the dechlorination step, the ALUGLU based catalysts have the highest hydrogen productivity. Particularly, ALUGLU presents a hydrogen productivity close to 2000 NI h⁻¹ kg_{cat}⁻¹ at 360 min of TOS. The ALUSUC based catalyst on the other hand, shows greater resistance to deactivation, more than double lifetime, but lower productivity, close to 1000 NI h⁻¹ kg_{cat}⁻¹ at 360 min of TOS. In both materials, the dechlorination treatment decreases the productivity but gives a small improvement in the stability of catalyst activity with time.

The composition of the gas stream was been determined at periodic intervals, and the results are expressed as hydrogen purity in Fig. 3. In all cases the hydrogen purity exceeds 98%, although catalysts using the ALUSUC support show a tendency to higher purity values (>99 vol.%). In both cases, hydrogen purity is higher

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Reaction performance and activity parameters.

Sample	H ₂ conc. (vol.%) ^a	Lifetime to 1000 Nl (h)	Lifetime to O NI (h)	Deactivation factor (NI h ⁻¹)
ALUGLUPtSn	97.6	15.0	24.1	109
ALUSUCPtSn	98.8	2.1	47.8	22
JM-Ref	97.2	3.5	11.0	134
ALUGLUPtSn D	97.9	6.8	16.8	99
ALUSUCPtSn D	99.1	0.5	24.4	36

^a Value at TOS- 240 min.



Fig. 4. X-ray diffraction patterns of fresh samples of ALUGLUPtSn and ALUSUCPtSn.

than that obtained with the catalyst prepared using a commercial alumina support. The composition of the gaseous outstream is summarized in Table 2. All the compositions give an average value of 98.5 vol.%, H₂ Small amounts of light hydrocarbons are detected, mainly methane. The dechlorination treatment slightly increases the hydrogen purity.

The presence of chloride species can play an important role in the Pt–Sn couple and their catalytic activity in reforming and dehydrogenation reactions. On the one hand, Cl is known to complex with Pt–Sn [21], and increase the interaction between the active phase and the support. On the other hand, Zhang et al. [22] concluded that the dechlorination process decreases the interaction between Pt and Sn, and destroys the initial matching between the metallic functions and the acid function of the fresh catalyst. This effect could lead to a strongly reduced catalyst activity after the dechlorination treatment.

3.2. Characterization

X-ray diffraction profiles of synthesized materials are shown in Fig. 4. Only diffraction lines assigned to γ -alumina (ISCD#01-077-0396) at 37.7, 45.8 and 66.9° (2 θ) and metallic Pt (ISCD#01-087-0644) at 38.6, 45.0, 65.5 and 78.3° (2 θ) are detected. Diffraction lines are broad, indicating the small size of the crystallites. Using the Scherrer equation, an average value of 4 nm is obtained for Pt domain size, using the main diffraction line at 38.7°. Pt_xSn phases are not directly detected by XRD, and this is consistent with observations of their formation in situ using operando Mössbauer spectroscopy [24]. Adsorption–desorption isotherms of fresh catalysts are plotted in Fig. 5. The isotherms are of type IV in the

Table 2

Composition of gas phase outstream at 240 min time on stream.

Sample	H ₂ (vol.%)	CH4 (vol.%)	Othersa
ALUGLUPtSn	97.6	1.4	0.6
ALUSUCPtSn	98.8	0.8	0.6
JM-Ref.	97.2	0.9	1.9
ALUGLUPtSn D	97.9	1.7	0.4
ALUSUCPtSn D	99.1	0.6	0.3

^a C₂-C₄ range hydrocarbons.

Table 3

Textural and surface properties of supports and catalysts



Fig. 5. Adsorption–desorption N_2 isotherms and pore size distributions of ALUGLU, ALUSUC and prepared catalysts.

IUPAC classification, showing a hysteresis loop. Extensive use has been made of surfactants to generate high surface area and control pore dimensions, [25,26] while the use of glucose [20] and sucrose is attractive both from economic and environmental viewpoints. Acidic pH due to hydrolysis of Al(OH)₆³⁺ species promotes sucrose hydrolysis to fructose and glucose, enhancing the pore size and the distribution, as observed in Fig. 5. Pore size distributions in the ALUGLU and ALUSUC materials are different, but both are centred at around 10 nm. In case of ALUSUC, a bimodal pore size distribution is observed, due to the presence of glucose and fructose. No evident changes in the shapes of the adsorption isotherms, mean pore sizes or pore size distribution are observed after impregnation, only a reduction of surface area and pore volume (Table 3). The use of glucose and sucrose thus leads to two alumina based supports with different textural properties, which strongly affect the catalytic performance, as shown in Fig. 2 and Table 1.

TEM micrographs of ALUGLUPtSn and ALUSUCPtSn are shown in Fig. 6. Both materials show the same structure, nanosized agglomerated particles of alumina with a size between 3 and 5 nm, and the porosity of the support is clearly visible. Dark spots are observed, that could be assigned either to alumina particles or Pt clusters. The pore and metal particle size that can be measured are consistent with the values shown in Table 3.

The chemical composition has been studied using X-ray fluorescence in order to quantify the amount of chloride present on the as prepared and treated catalysts. In both ALUGLUPtSn and ALUSUCPtSn, the total amount of Cl is around 1.2 wt%. After steam treatment, this value decreases to 0.5–0.6 wt%. For reference, the amount of chloride ion present in as prepared ALUGLU and ALUSUC supports was also measured, and an average Cl value of 0.3 wt% was determined. These values are in line with those described elsewhere [22].

 NH_3 -TPD profiles of ALUGLU and ALUSUC materials are shown in Fig. 7. These profiles are characterized by two main peaks, one

Sample	$S_{BET} (m^2 g^{-1})$	Vp (cm ³ g ⁻¹)	$D_{\rm p}$ (BJH, nm) ^a	Metallic disp (%)	Total acidity (μmol NH ₃ g ⁻¹)
ALUGLU	273	0.66	7.5	5 -5 1	437
ALUGLUPtSn	227	0.54	7.1	65	327
ALUSUC	197	0.43	7.2	-	462
ALUSUCPtSn	153	0.37	7.4	69	273
JM-Ref.	130	0.25	12.0	53	120

^a Calculated from adsorption branch data.

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Fig. 6. TEM micrographies of prepared catalyst. Left: ALUGLUPtSn; Right: ALUSUCPtSn.



Fig. 7. Comparison of the evolution of NH3-TPD profiles of studied materials. Left: ALUGLU materials; Right: ALUSUC materials.

centred close to 200 °C, which signals the presence of Brønsted type acid sites, and a second peak between 300 and 400 °C assigned to Lewis type acid sites. Incorporation of the active phase on the support decreases the number of acid sites, probably due to partial coverage of the sites and interaction with metal species. Total acidity values are provided in Table 3. After dechlorination, the total acidity decreases for ALUGLUPtSn D to 292 µmol NH3 g-1 and for ALUSUCPtSn D to 256 µmol NH3 g⁻¹, compared with initial values of 327 and 273 µmol NH₃ g⁻¹, respectively. The acidity decrease can probably be explained as a combination of two phenomena: sintering and phase transformation. These phenomena start at as low as 600 °C in the case of commercial y-alumnia, followed by structural transformations [27,28], which provoke a decrease of the number of Lewis acid sites and weakens the interactions between the support and the active phase [22], and elimination of CI [23]. Dechlorination decreases the hydrogen productivity of the catalysts in partial dehydrogenation of ULSK as shown in Fig. 2, but increases stability due to an acidity modification, as noticed. From the acidity data in Table 3, it may be concluded that a medium acidity is required for higher hydrogen productivity, higher or lower values giving less productivity but lower deactivation rates. It is of interest to relate the relative acidity of the supports to the hydrogen purity described above: the ALUGLU catalysts produce slightly lower purity hydrogen, probably a result of increased cracking reactions due to the higher number of acid sites; similarly the lower surface acidity of ALUSUC based catalysts leads to a higher purity hydrogen product.

In the TPR analysis performed on the fresh catalysts, two broad peaks are observed (Fig. 8). For ALUGLUPtSn, a first peak with a maximum at 220 °C (shoulder at 180 °C) is seen, and a second peak with a maximum at 600 °C and ending at 640 °C. The reduction of Pt(IV) takes place normally in a temperature range of 150–300 °C depending on the strength of the interaction with the support. In the present case, the first peak is interpreted as including a contribution from the first reduction peak of Sn(IV) and the reduction of Pt(IV) [16,17]. The reduction of Sn(IV) normally leads to two thermal reduction peaks at 200–300 °C and 380–600 °C so that the shoulder at 180–200 °C and the second broad peak at 600 °C could be attributed to the reduction of Sn species [17,29,30]. The profile obtained for ALUSUCPtSn is similar, but with a shift of the peaks to 300 °C and 550 °C, respectively, indicating the Sn(IV) species to be more easily reduced. These different reducibility patterns are related to the textural properties of the support [31], in particular to the lower pore volume of the ALUSUC catalyst (0.37 cm³ g⁻¹) than that of ALUGLU (0.54 cm³ g⁻¹). The lower surface area and pore volume facilitates reduction of Sn species but



Fig. 8. H₂-TPR profiles of ALUGLUPtSn and ALUSUCPtSn. Heating rate: 10°C min⁻¹.



Fig. 9. TGA-DTA analysis of ALUSUCPtSn used catalyst.

favours a stronger interaction between Pt and Sn, which is reflected in the increase of the Pt reduction peak temperature from 220 to 300 °C. This increment in Pt reduction temperature may affect the nature of the final alloy and the resulting catalyst performance, giving lower hydrogen productivity as is observed for ALUSUC based catalyst.

The TGA analyses performed on the spent catalysts show a weight loss in the range 320-480 °C, attributable to the combustion of the carbon coke formed during the PDh reaction. As a representative example, TG and DTA plots of spent ALUSUCPtSn are presented in Fig. 9. The values of mass loss in percentage are in the range of 3-7% and the carbon amount formed appears to correlate with the deactivation factor for each catalyst. From the DTA analysis, two different peaks ascribable to the combustion of different types of carbon may be distinguished. The peak at 360 °C is related to the carbon coke formed on the active metal phase of the catalyst and the second peak at 460-480 °C results from the combustion of the carbon coke formed on the acid sites of the alumina support [32,33].

The TGA plots of spent catalysts (Fig. 10) indicate similar behaviour in all cases, but with lower weight losses for the dechlorinated materials. There is a direct correlation with the acidity and coke formation, less intense peaks being observed for the dechlorinated catalyst and a slight displacement of the maximum temperature in the second peak to higher temperatures, probably related the support acidity. The degree of graphitization of the



Fig. 10. DSC curves of spent catalysts. (a) JM-ref. (b) ALUGLUPtSn, (c) ALUSUCPtSn, (d) ALUGLUPtSn D, (e) ALUSUCPtSn D, (f) JM-ref.

coke deposited could affect the rate and extent of deactivation [34]. Further studies are underway to improve understanding of the deactivation effects due to carbon deposition.

4. Conclusions

γ-Alumina supported PtSn catalysts are active in the partial dehydrogenation of ultra low sulfur kerosene (ULSK) under mild pressure (10 bar) and temperature (450 °C). The materials synthesized using glucose and sucrose templates, and used as support for the Pt-Sn active phase, provide greater H₂ productivity than is obtained by impregnation of a commercial alumina support. The hydrogen productivity, catalyst deactivation rate and catalyst lifetime are strongly dependent on catalyst textural properties. Mild acidity, easily reducible active phases and high surface area in a Pt-Sn based mesoporous alumina catalyst appear favourable to PdH of ULSK.

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Methodology to define gasoline surrogates dedicated to auto-ignition in engines

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ABSTRACT

A methodology to define proportions of compounds in gasoline surrogates dedicated to auto-ignition modelling in engines is described. Based on auto-ignition properties and global atom content of the reference gasoline, this methodology provides surrogates nearing gasoline auto-ignition in engine but also gasoline density or lower heating value. Increasing the number of surrogate compounds induces a convergence of the mixture defined according to the methodology towards the classification into chemical families of the gasoline to emulate, which is a key for pollutant emission representativity. Applied to a European unleaded gasoline with an octane rating of 95, a ternary surrogate made of 13.7% of *n*-heptane (by mole fraction), 42.8% of isooctane and 43.5% of toluene is obtained. The direct experimental comparison of this surrogate and of the reference gasoline in an engine operated in Controlled Auto-Ignition (CAI) combustion mode confirms the global validity of the approach (auto-ignition timing but also power output, efficiency and pollutant emissions). The selected operating point for this comparison is also modelled with 3D CFD to demonstrate that the final aim of gasoline emulation in engine codes with such a surrogate can be successfully reached.

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1. Introduction

Gasoline auto-ignition has always been an important research subject because of destructive risks linked with engine knocking. Moreover, in last two decades, understanding and controlling gasoline auto-ignition have become, by itself, a way to improve engine efficiency through new low-temperature combustion modes such as Homogeneous Charge Compression Ignition [1] and Controlled Auto-IgnitionTM ([2] – CAI). In order to represent these combustion modes with CFD codes, auto-ignition kinetics is a key point that must be accurately modelled.

This issue is complex because commercial gasolines contain a full spectrum of compounds which details depend on the crude origin and the oil refinery process. Moreover, defining a universal composition is illusive because gasoline differs from country to country and its composition is ever changing. For example, only considering European Union countries, legislation leads to distinct compositions in Southern and Northern countries at any given time as well as distinct compositions during summer and winter at a given place, despite similar properties in terms of octane rating, lower heating value or density.

To overcome this difficulty, representative and simple mixtures of a few compounds, namely surrogates, are generally used to emulate fuel behaviour. Compound selection is based on their fundamental chemical or physical properties in relation with the modelling goals. Blending proportions aim to match a precise target property, either on the physical side (density, evaporation characteristics, etc.), or on the chemical side (auto-ignition delay, flame speed, propensity to induce some pollutants, etc.). For example, Zhang et al. [3] have defined a surrogate for soot modelling which composition is based on the propensity of each compound to produce the right amount of soot precursors.

Generally speaking, isooctane is the simplest surrogate for gasoline. It is often used for flame propagation studies [4] but it is not representative for auto-ignition because of its high octane numbers. To match a gasoline octane number, *n*-heptane is mixed with isooctane to form Primary Reference Fuels (PRFs). Such binary mixtures are not either satisfactory surrogates because different PRF mixtures are needed to match the gasoline auto-ignition behaviour on different engine operating conditions [5–7]. Leppard [5] has related this fact to a marked different behaviour between, on the one hand, linear and branched paraffinic fuels (such as PRFs) and, on the other hand, other chemical families, accounting for about half the content of an actual gasoline.

The deviation in auto-ignition behaviour between linear or branched paraffins and any other fuel is called the sensitivity and is quantified as the difference between the compound Research Octane Number (RON) and the compound Motor Octane Number (MON). Since up to 50% of an actual gasoline is made out of fuels that are neither linear nor branched paraffins, gasoline has an important sensitivity of about 10. A way to introduce sensitivity in gasoline surrogates is to add non-paraffinic compounds to PRF mixtures.





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The most widely used surrogate type with non-paraffinic compound(s) is the mixtures of isooctane, *n*-heptane and toluene, called Toluene Reference Fuels (TRFs) [8–10]. Measurements in shock tube [8] as well as in engine [9] have proved their ability to behave like gasoline from auto-ignition standpoint. Because of their suitability as gasoline surrogate, numerous experimental and numerical studies have been dedicated to the improvement of the knowledge of their kinetics [9,11]. The similarities with gasoline behaviour and the availability of various validated detailed chemistry mechanisms have turned TRF mixtures into one of nowadays best gasoline surrogates for auto-ignition purpose [4].

More complex surrogates involving numerous compounds exist but the validation of their detailed chemistry mechanisms is only partial with respect to engine conditions. For argument's sake, Fikri et al. [12] have proposed a surrogate containing diisobutylene in addition to TRFs while Yahyaoui et al. [13] have proposed surrogates containing isooctane, toluene, 1-hexene and Ethyl *tert*-Butyl Ether (ETBE).

To the authors' knowledge, despite the publication of numerous surrogate compositions, no clear methodology to define the compound proportions has ever been published. Some surrogates are defined matching a particular target property (for example, an octane number) but there is no clear explanation about the way the other degrees of freedom in the choice of compound fractions are managed. The present paper aims to formulate a general framework for the definition of surrogate compositions dedicated to the emulation of the auto-ignition of gasoline in engines.

The definition of a surrogate first requires a precise knowledge of the target fuel to emulate. Therefore, a statistical analysis of the reference gasoline has been performed with gas chromatography and the results are detailed in the next section. In the following sections, the methodology is presented and split into two main parts: the choice of the relevant surrogate compounds and the selection of precise constraints to compute the compound proportions. Finally, the methodology is applied to the reference gasoline and the resulting surrogate is experimentally compared in an engine to the reference gasoline. The selected operating point for this comparison is also modelled with 3D CFD to demonstrate that the final aim of gasoline emulation in engine codes with such a surrogate can be successfully reached.

2. Reference gasoline from the 2005-2009 period

The definition of a fuel surrogate first requires the identification of a reference composition for the target fuel. Previous studies [6,8,14] have already provided information about reference European or American gasolines and identified their main compounds but these gasolines do not match the gasoline available for our engine tests. In the present study, the aim is to emulate a RON 95 unleaded gasoline sold in France and certified according to the EN 228 specification for the 2005–2009 period without any distinction between summer-grade and winter-grade fuels. An analysis of the reference gasoline has therefore been performed as a first step to define a relevant surrogate.

Numerous samples of commercial gasolines from this period have been collected and analysed with gas chromatography to obtain a statistically-relevant composition of an "averaged gasoline" denoted ULG95. This analysis provides a global classification of gasoline compounds into chemical families but also a detailed speciation of all compounds with significant concentration. Fig. 1 and Table 1 summarise the results of this analysis. Fig. 1 provides an information about the deviation of the compositions around the average classification into chemical families. Table 1 details this average classification and indicates the concentration of the two



Fig. 1. Classification of ULG95 compounds into chemical families (gaseous chromatography analysis); squares indicate mean composition (averaging over numerous samples from the 2005–2009 period); lines indicate scattering; S and W indicate mean cyclic paraffin content in the summer-grade and winter-grade samples, respectively.

most important compounds of each chemical family (except for aromatics where the focus is on benzene, a regulated compound).

Linear paraffins account for about 10.7 mol% of ULG95 with *n*-pentane and *n*-heptane as most significant compounds. *n*-Pentane is the single most important linear paraffin in the gasoline (about 4.1 mol% of ULG95) and represents about 39 mol% of the total amount of linear paraffins. *n*-Heptane is the second most important compound (3.3 mol% of ULG95) and represents the same amount of linear paraffins (about 30 mol%) as all other minor linear paraffins together. These individual compound contents are in close agreement with the available data in the literature [8,14].

Branched paraffins is the largest chemical family in ULG95 (about 35.1 mol% of gasoline) and is made of a wide range of individual compounds. Isopentane (2-methylbutane) is the single most important branched paraffin (about 11.1 mol% of ULG95, *i.e.* 32 mol% of branched paraffins). The second one is isooctane (2,2,4-trimethylpentane) at about 6.9 mol% of gasoline (20 mol% of branched paraffins); this concentration is more than 3 times higher than that of any other branched paraffin. Again these data are in close agreement with the composition of the published European gasolines [6,14] but indicates higher concentrations than in the American reference gasoline of Gauthier et al. [8].

Cyclic paraffins (10.9 mol% of ULG95) are almost exclusively made of cyclopentane (8.5 mol% of gasoline, i.e. 78 mol% of cyclic paraffins) and of cyclohexane (0.9 mol% of gasoline, i.e. 8 mol% of cyclic paraffins). It is noteworthy that statistics on cyclic paraffins show a large variance (Fig. 1). Nevertheless, separating the wintergrade gasoline samples from the summer-grade gasoline samples, the distribution of cyclic paraffins appears to be the addition of two narrow distributions, the means of which are denoted S (summer) and W (winter) in Fig. 1. Furthermore, the variations in cyclic paraffin concentration are compensated by a variation in branched paraffins, the sum of both chemical family concentrations being fairly similar in all samples (deviation of less than 4 mol%). In the European gasoline of Håkansson et al. [14], the single most important cyclic paraffin is cyclohexane that has similar concentrations as cyclopentane in the present study. In the reference American gasoline of Gauthier et al. [8], cyclopentane is the most abundant compound in the whole gasoline (16.8 mol%) and has a concentration that closely matches our typical summer-grade gasolines. Finally, in the European gasoline of Kalghatgi [6], the concentration in cyclic paraffins is representative of one of our winter-grade gasoline samples.

Aromatics is the second largest chemical family (about 31.7 mol% of ULG95) with toluene as main species (11.7 mol% of gasoline and 37 mol% of aromatics). All other aromatic compounds represent less than 10 mol% of this chemical family. Benzene is the only aromatic compound to have a specific content restriction (<1 vol%) in the EN 228 specification, which implies that it is a

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Table 1

Reference gasoline composition: classification into chemical families and main individual species. Values issued from numerous gaseous chromatography analyses on samples of French gasoline from the 2005–2009 period of the EN 228 specification.

Chemical family	Species	Content (mol%)	Content (vol%)
Linear paraffins		10.7	10.7
	<i>n</i> -Pentane	4.1	3.8
	n-Heptane	3.3	3.8
Branched paraffins		35.1	39.8
	Isopentane	11.1	10.3
	Isooctane	6.9	9.1
Cyclic paraffins		10.9	8.8
1996 - 1999 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	Cyclopentane	8.5	6.4
	Cyclohexane	0.9	0.8
Aromatics		31.7	31.2
	Benzene	0.6	0.4
	Toluene	11.7	9.9
Olefins		5.7	4.8
	2-Methyl-2-butene	1.7	1.4
	Cyclopentene	0.9	0.6
Oxygenated		5.9	4.7
	Ethanol	1.8	0.9
	MTBE	3.9	3.7

minor species in ULG95. The concentration in toluene is also in close agreement with the available data in the literature [8,14]. The globally larger content in aromatics in the Swedish gasoline of Håkansson et al. [14] is due to its belonging to the 2000–2005 period of the EN 228 specification that was more permissive for aromatics (<42 vol% authorised before 1st January 2005 and <35 vol% after).

Olefins is a minor chemical family (5.7 mol% of gasoline) that is further splitted into numerous isomers in the C_5 – C_6 range. The single most important olefin is 2-methyl-2-butene (1.7 mol% of gasoline but 30 mol% of olefins) and the second most important is a cyclic olefin: cyclopentene (0.9 mol% of gasoline and 16 mol% of olefins). No individual olefin compound appears in the published data from [8,14] but this may be explained by individual concentrations well below the level of the less abundant compound detailed in these papers.

Oxygenated compounds are additives from the refinery process intended to improve the octane rating of the crude oil. Their content is limited by the EN 228 specification (<2.7 mas% of oxygen atoms for the 2005–2009 period). There is generally no mix of oxygenated additives but the statistics in Table 1 indicate 30 mol% of ethanol and 67 mol% of MTBE in this family. As for cyclic paraffins, this is the result of the addition of two Dirac distributions: MTBE was the exclusive additive for the oldest gasoline samples and ethanol is the exclusive additive for the latest samples. Oxygenated compounds are absent from the compositions in [6,8,14] since these reference gasolines are purposely built without oxygenated additives.

3. Definition of gasoline surrogates for auto-ignition

The proposed methodology aims to define gasoline surrogates dedicated to auto-ignition with an objective of usage in engine modelling. Therefore, the surrogate composition is not exclusively dictated by the matching of auto-ignition delays but also by the nearing of other important physical properties of a gasoline with respect to engine operation (lower heating value, air to fuel ratio at stoichiometry, pollutants, etc.). Since most of these properties are intimately linked with the hydrogen, carbon and oxygen content in the fuel, the atomic content of surrogate compounds will appear as a major guideline. The building of a surrogate with such constraints has two steps. First, representative compounds must be chosen. Then, criteria to calculate their proportions need to be defined. These steps are detailed in the next two sections.

3.1. Choice of representative compounds

Representative compounds can be species present in the gasoline itself or belonging to characteristic chemical families. The choice of one compound rather than another is primarily based on its properties (representative of its family in terms of composition, auto-ignition delay, etc.). But a second important factor in the selection of a compound is the current knowledge of its chemical kinetics since the final goal is auto-ignition modelling in engines. This means that the selection of compounds made hereafter may evolve if the kinetics knowledge of a discarded but suitable species improves.

In order to guide the selection of representative compounds, the composition of ULG95 detailed in the previous section is used as a support. Gasoline mainly contains branched paraffins and aromatics that provide high octane numbers. For such families, the most obvious surrogate compounds are isooctane and toluene, respectively, for many reasons. First, isooctane and toluene are two high octane number compounds that are actually present in large quantities in gasoline (Table 1). Second, side properties of these compounds (hydrogen and carbon content, lower heating value, density, etc.) are reasonably close to gasoline. And last but not least, these species are among the few for which chemical kinetics have been extensively studied on a wide range of conditions representative of engine operation. It is noteworthy that toluene being the single most important aromatic, there is no alternative compound to include. On the other hand, isooctane is only the second most abundant branched paraffin and the inclusion of isopentane in surrogates is highly recommended as soon as fully validated mechanisms will be available. This inclusion would not only improve the kinetics representativity of the surrogate but also notably reduce the molar weight of the surrogate, which is one of the most obvious shortage of surrogates only built on C_7-C_8 compounds.

Linear paraffins is the third chemical family in importance in ULG95 (Table 1). The inclusion of a compound from this family is necessary to counter-balance branched paraffins and aromatics and to reach realistic auto-ignition properties. As a matter of fact, some branched paraffins and all aromatics are less prone to autoignite (in engine-related terms, have larger octane numbers) than the target gasoline while liquid linear paraffins are very prone to auto-ignite (in engine-related terms, have very low octane numbers). Keeping in mind the will to near ULG95 content, there are only two linear paraffins to consider: n-pentane and n-heptane. n-Heptane appears to be the most suitable compound for two important reasons: its low octane numbers and the knowledge of its kinetics. The octane numbers of n-heptane are zero (by definition) while those of *n*-pentane are about 62 [15]. Therefore, the usage of *n*-pentane as representative of linear paraffins to counter-balance the high octane numbers of isooctane and toluene would imply a content in linear paraffins in the surrogate well above that in ULG95. Furthermore, n-heptane is certainly the large hydrocarbon for which chemical kinetics is best known and the amount of well-validated, published mechanism is the largest.

A mixture of *n*-heptane, isooctane and toluene as a first step to build a gasoline surrogate is a widespread choice [4,8–10]. This choice is first dictated by the current knowledge of chemical kinetics [4] but also by the belonging of these compounds to the major gasoline chemical families and the possibility to grossly recover most of gasoline properties. In order to improve gasoline surrogates, the accounting for more chemical families (olefins, oxygenated compounds and/or cyclic paraffins) is necessary.

With more compounds, it is possible to reproduce more gasoline properties (for example, oxygen content or molar mass) and to near the decomposition into chemical families. Keeping n-heptane, isooctane and toluene as the core compounds, the additional species should be chosen so that surrogate properties tend towards gasoline properties. More specifically, additional compounds should be lighter than gasoline since the core compounds are either as heavy or heavier than gasoline, impeding the surrogate molar mass representativity. Similarly the RON or MON value of additional compounds should be similar to that of gasoline while the compound sensitivity should be higher than the one of gasoline. The similar RON or MON aims not to distort the equilibrium between the main family representatives when matching gasoline RON or MON. The larger sensitivity allows to simultaneously near both RON and MON, which is not possible for most TRF mixtures due to the large content in non-sensitive fuels (n-heptane and isooctane). Matching both octane numbers is important to recover the long-known difference in auto-ignition behaviour between actual gasolines and PRFs [5,6].

Oxygenated compounds is a minor chemical family in ULG95 but with very specific properties and an importance that will grow in the near future. Oxygenated compounds are additives introduced during the production of gasoline from crude oil, restricting the compound choice to a few, mainly ethanol, Methyl *tert*-Butyl Ether (MTBE) and Ethyl *tert*-Butyl Ether (ETBE). From a surrogate point of view, ethanol has the advantage to be lighter and to have much well-known chemical kinetics. The addition of ethanol is therefore recommended. This choice has the further advantage to be in line with European Union plans to introduce more ethanol within gasoline. Definition of surrogates for gasoline and its mixtures with ethanol would therefore only be a matter of ethanol fraction.

Cyclic paraffins is a chemical family with a molar fraction as large as the proportion of linear paraffins in ULG95. Cyclic paraffins are key compounds for the formation of aromatic pollutants [3,16– 18] that can lead to soot growth [3,17,19]. The only major cyclic paraffins present in ULG95 are cyclopentane and cyclohexane, which both match the constraints of lightness and octane number range prescribed hereabove. They are also major compounds in the reference gasolines of Håkansson et al. [14] and of Gauthier et al. [8] and are therefore generally-valid representatives. Since the chemical kinetics of cyclohexane are better known [16,17,19–26] than that of cyclopentane [16,21,23,27], this compound is recommended for the near-term. Progress in the knowledge of cyclopentane kinetics could lead to a shift to this compound in the long-term. Nevertheless, it should be stressed that the massive introduction of a C_5 compound (about 10 mol% of ULG95) should be compensated by the introduction of heavier aromatics (for example, xylenes) to be able to match gasoline molar mass.

Olefins is a minor chemical family in ULG95 but evidences suggest that the accounting for this chemical family is a key feature when gasoline soot propensity is looked after [3,18,28]. Compounds that are lighter than gasoline and with similar octane numbers are only a few among C₅ and C₆ isomers. 1-Hexene [13] and diisobutylene [12] are species that are often met in gasoline surrogates but do not match these constraints: 1-hexene has too low octane numbers and diisobutylene is too heavy. Branched olefins are more often met in gasolines than cyclic olefins but only the kinetics of cyclohexene [17,20,28,29] has been widely studied. Alternative compounds have only received few attention today from the auto-ignition kinetics point of view: cyclopentene has been studied in [27,30] and 1,3-cyclohexadiene in [17,20], while 2-methyl-2-butene has only been tested in [31]. Cyclohexene has the further advantage to bring a splitting into chemical families that precisely matches that of ULG95. Therefore, cyclohexene is recommended for the near-term but any major progress in the kinetics knowledge of 2-methyl-2-butene or cyclopentene (the most abundant olefins in ULG95) should lead to a reconsideration of this choice.

3.2. Constraints for proportion definition

Once surrogate compounds have been selected, proportions must be unambiguously defined with precise constraints. In the present study, the focus is on the emulation of a reference gasoline in terms of auto-ignition process in internal combustion engines. Therefore, the chosen constraints are first values quantifying gasoline auto-ignition propensity in engines, namely the Research Octane Number (RON) and the Motor Octane Number (MON). Gasoline differs from other hydrocarbon mixtures such as jet fuel or Diesel by its density, its distillation curve (the consequence of the compound boiling points), its lower heating value or its molar mass. The density, the boiling point, the lower heating value and the molar mass of any compound are all dependent on the species atomic content and on the species belonging to a particular chemical family [15]. As a consequence, the second set of constraints for the definition of compound proportions is the content in carbon, hydrogen and oxygen atoms since the belonging to chemical families is already met through compound selection.

The quantification of auto-ignition propensity in engines is a difficult task because the auto-ignition process is heavily dependent both on the fuel nature and on the operating conditions. To help classify the fuels, two normalised tests have been defined for standard spark-ignition operation, leading to the RON and MON values. It is long known [5] that the RON and MON values only provide two approximative classifications of auto-ignition propensity that can be undermined under specific engine conditions [6,7]. Nevertheless, these quantities can still be used as a reference if the influences of the fuel nature and of the operating conditions are separated out. A proper distinction of these influences can be obtained defining an Octane Index (OI) following:

$$OI = (1 - K) \times RON + K \times MON = RON - K \times S$$
(1)

where the *K* factor sums up the influence of the operating conditions and S = RON - MON is the fuel sensitivity [6]. This OI provides a clear classification of engine performances when considering results from different fuels and different engines, which cannot be reached only based on the RON and MON values [6]. With the

Z

K factor introducing the dependence on the operating conditions, the RON and MON values bring a proper information about the only influence of the fuel. Consequently, the RON and MON values appear as attractive, simple and widespread quantities for the characterisation of a hydrocarbon mixture.

Eq. (1) indicates that the gasoline auto-ignition propensity on any actual operating point is dependent on both the RON and the MON values, or alternatively on both the RON and the sensitivity values. The creation of a gasoline surrogate valid for a large set of operating points therefore requires compounds with sensitivity, *i.e.* compounds that are not either linear paraffins nor branched paraffins.

Describing the auto-ignition propensity is not enough to develop combustion models suitable with today's demands. More and more stringent pollutant emission regulations require a precise description of the combustion process and of any relevant side phenomena (for example, fuel droplet dynamics in direct injection engines). To reach such a goal, other surrogate properties have to be in close agreement with gasoline properties. To be able to accurately predict the overall heat release, the surrogate lower heating value must agree with that of gasoline. To properly describe the liquid phase of a jet, the surrogate droplet momentum has to be in accordance with the actual gasoline droplet dynamics which at least requires a proper ratio between the injector volumetric flow rate and the droplet mass kinetic energy, i.e. the fuel density. The air to fuel mass ratio at stoichiometry has to be correctly reproduced to ensure a similar fuel/air equivalence ratio with gasoline and its surrogate. All these properties are mainly dependent either directly on the atomic content in hydrogen, carbon and oxygen (air to fuel ratio) or mainly on the chemical family and the hydrogen to carbon ratio (lower heating value, boiling point, density).

An accurate information about the pollutant emissions (CO, NO_x, soot and unburned hydrocarbons) and the greenhouse gas emissions (mainly CO₂) is also only reachable if the global atomic content of the reference fuel is matched by the surrogate. Namely, the ratio between hydrogen and carbon atoms (H/C ratio = y/x) in the surrogate is central to ensure an accurate quantification of the carbon-containing species mass fractions as can be seen in Eq. (2) written for lean to stoichiometric mixtures.

$$\begin{split} \phi \mathsf{C}_{\mathsf{x}}\mathsf{H}_{\mathsf{y}}\mathsf{O}_{\mathsf{z}} + \mathcal{R}\mathsf{O}_{2} + \alpha \mathcal{R}\mathsf{N}_{2} &\to (x\phi(1-\gamma) - a\beta)\mathsf{C}\mathsf{O}_{2} + x\phi\gamma\mathsf{C}\mathsf{O} \\ &+ \beta\mathsf{C}_{a}\mathsf{H}_{b} + \frac{y\phi - b\beta}{2}\mathsf{H}_{2}\mathsf{O} \\ &+ \left(\mathcal{R}(1-\phi) + \frac{x\phi\gamma}{2} + \frac{\beta}{4}(4a+b)\right)\mathsf{O}_{2} \\ &+ \alpha \mathcal{R}\mathsf{N}_{2} \end{split}$$
(2)

where $\mathcal{R} = (x + \frac{y}{4} - \frac{z}{2})$ is the molar oxygen to fuel ratio to reach stoichiometry, ϕ is the mixture fuel/air equivalence ratio and α is the nitrogen to oxygen molar ratio in air ($\alpha \sim 3.76$).

For any surrogate complexity, a last inescapable constraint is unity for the sum of the compound fractions. This reduces to (n - 1) the number of physical targets of a surrogate with *n* compounds. It is noteworthy that targetting the atomic content rather than specific targets like the lower heating value or the density allows to better approximate more quantities as many of them are intimately related to the H/C ratio.

The calculation of a surrogate composition requires the mathematical formulation of the selected constraints. The atomic content constraints may be individually expressed for hydrogen, carbon and oxygen or alternatively as the H/C ratio, the O/C ratio and the molar mass. Since the influence of the H/C ratio, the O/C ratio and the molar mass on the other properties are more significant than atomic contents alone, they are preferably selected. Therefore, the system for a 6-compound surrogate may be written as:

$$\sum_{i=1}^{n} x_i = 1 \tag{3}$$

$$\sum_{i=1}^{n} x_i H_i = H/C$$

$$(4)$$

$$\sum_{i=1}^{n} x_i O_i = 0/C \tag{5}$$

$$\sum_{i=1}^{n} x_i \mathcal{M}_i = \mathcal{M} \tag{6}$$

$$\sum_{i=1}^{n} f(x_i, RON_i) = RON$$
(7)

$$\sum_{i=1}^{n} g(x_i, MON_i) = MON$$
(8)

where *n* is the number of compounds in the surrogate, x_i is the molar fraction of species *i*, H_i , C_i and O_i are the number of hydrogen, carbon and oxygen atoms in species *i*, respectively, M_i is the molar weight of species *i* while RON_i and MON_i are the RON and MON values for species *i*, respectively.

The functions $f(x_i, RON_i)$ and $g(x_i, MON_i)$ have multiple expressions in the literature because the octane number of a mixture of fuels is not simply the average of compound values weighted by the volume fractions. Nevertheless, as demonstrated in Appendix A, an averaging of compound values weighted by molar fractions provides as accurate results as more complex formula from the literature. Therefore, for the computation of surrogate compositions in the present paper, the relations $f(x_i, RON_i) = x_i RON_i$ and $g(x_i, MON_i) = x_i MON_i$ are used. Of course, anyone may choose any other correlation to express the constraints about octane numbers and still apply the methodology.

4. Application of the methodology

As an illustration, the methodology is applied to ULG95 selecting different levels of surrogate complexity. These different levels are defined by the choice of the number of compounds and by a priorisation of the constraints.

As already detailed above, TRF mixtures are nowadays the best trade-off between surrogate representativity and accurate knowledge of chemical kinetics. Therefore, a first ternary surrogate based on *n*-heptane, isooctane and toluene is defined and denoted Sur95t. Then, as the inclusion of oxygenated compounds is required to define surrogates for gasoline and its mixtures with ethanol, a quaternary surrogate including the first three compounds and ethanol is defined and denoted Sur95o. Finally, all chemical families are considered in a senary surrogate (six compounds) denoted Sur95f by the addition of cyclohexane and cyclohexene.

Based on Eq. (1), it can be stated the accurate representation of the Research Octane Number and a proper approximation of the gasoline sensitivity are enough to build a surrogate that is representative from the auto-ignition point of view. Therefore, the RON constraint is selected as the most important while the MON constraint is set at the end of the list as long as the defined surrogate has a sensitivity similar to that of gasoline.

Properties such as the lower heating value, the boiling point or the density are mainly dependent on the H/C ratio and on the chemical family, rather than directly on the content in carbon and hydrogen. Furthermore, as long as gasolines with low oxygen content are considered, the H/C ratio is more important than the O/C ratio for the definition of the air to fuel ratio at stoichiometry and of the pollutant fractions. Therefore, the H/C ratio is put at the top of the constraint list and the molar mass at the end of it.

With such a priorisation, the composition of the ternary surrogate Sur95t is computed with Eqs. (3), (4) and (7) as constraints. The composition of the quaternary surrogate Sur95o is obtained with the same constraints plus Eq. (5) to accurately incorporate the oxygen content. Finally, the computation of the senary surrogate composition uses all constraints defined by Eqs. (3)–(8). The resulting compositions are detailed and compared with that of gasoline in Table 2. In addition, the surrogate target properties as well as the lower heating value and the density are compared to those of gasoline in Table 3 to emphasize the similarity of other properties.

The surrogate compositions indicate that a ternary surrogate is already enough to grossly recover the classification of gasoline compounds into chemical families (Table 2). Adding new compounds allows to further near this classification which is important when pollutant formation is considered [3,17-19]. In addition to the classification into chemical families, surrogates also near the main gasoline properties (Table 3). Gasoline sensitivity is already well recovered for the ternary and quaternary surrogates even if it is not a constraint for the compound proportion definition. Furthermore, the density and the lower heating value are in close agreement with those of gasoline for all surrogates. On the other hand, the surrogate molar mass is overestimated for the least complex surrogates because of the massive introduction of relatively heavy compounds and improves when light additional compounds are integrated. It is noteworthy that the restriction about aromatic content in gasoline imposed by the EN 228 specification (<35 vol%) is respected for all surrogates without any addition of a specific constraint.

5. Validation of the methodology

Since the target is engine modelling for which a well-validated kinetics scheme is needed, only TRF mixtures are considered for the methodology validation.

Table 2

Compositions in molar fractions of ULG95 (averaging over numerous gaseous chromatography analyses of samples from the 2005–2009 period of EN 228 specification) and of the proposed surrogates.

Gasoline	ULG95 (%)	Surrogate	Sur95t (%)	Sur950 (%)	Sur95f (%)
Linear paraffins	10.7	n-Heptane	13.7	15.8	11.4
Branched paraffins	35.1	Isooctane	42.8	34.3	28.1
Cyclic paraffins	10.9	Cyclohexane	-	-	10.2
Aromatics	31.7	Toluene	43.5	42.3	35.5
Olefins	5.7	Cyclohexene	-	-	7.4
Oxygenated	5.9	Ethanol	-	7.6	7.4

Table 3

Main properties of ULG95 (averaging over numerous gaseous chromatography analyses of samples from the 2005–2009 period of EN 228 specification) and of surrogates defined in Table 2.

	ULG95	Sur95t	Sur95o	Sur95f
Research Octane Number	95.0	95.0 ^a	95.0 ^a	95.0 ^a
Motor Octane Number	85.0	87.8ª	86.0 ^a	85.0 ^a
H/C ratio	1.801	1.801	1.801	1.801
O/C ratio	0.011	0.000	0.011	0.011
Molar weight (g/mol)	94.3	102.7	97.5	94.3
Density at 298 K (kg/m ³)	749	750	755	763
Lower Heating Value (k]/kg)	42801	42893	42229	42247

^a Research and Motor Octane Numbers of surrogates are computed according to Eq. (A.4).

The methodology is first proofed against shock tube measurements available in the literature. To the authors' knowledge, measurements of Gauthier et al. [8] are the only available and detailed data. Unfortunately, these measurements have not been performed for a premium grade European gasoline but for a reference American regular gasoline. Since authors were unable to perform shock tube measurements for ULG95, a surrogate for the American gasoline of Gauthier et al. [8] is defined according to the methodology and compared to the published data.

Then, to specifically validate the ternary surrogate for ULG95, a direct experimental comparison of ULG95 and Sur95t in an engine is performed. Furthermore, the selected operating point is also modelled with 3D CFD to prove that the final goal of gasoline emulation for simulation can be reached (see Section 6).

5.1. Validation based on shock tube data

Gauthier et al. [8] have studied the auto-ignition of a reference gasoline denoted RD387 and defined by General Motors as representative of an American regular gasoline. RD387 has an Anti-Knock Index, AKI = (RON + MON)/2, of 87 and a H/C ratio of 1.85 [8].

The shock tube measurements of Gauthier et al. [8] are restricted to temperatures above 800 *K* because of the measurement technique. This prevents from testing the sensitivity of auto-ignition to the surrogate composition at lower temperatures. Nevertheless, this temperature domain is similar to the one locally encountered within the engine at the onset of knock or during CAI combustion mode. Therefore, these measurements are valuable for engine study.

Gauthier et al. [8] have proposed two surrogates for RD387 which compositions by molar fraction are 16.9%/55.6%/27.5% (Gauthier A) and 17.4%/62.7%/19.9% (Gauthier B) of *n*-heptane, isooctane and toluene, respectively [8]. They have experimentally demonstrated that auto-ignition delays of these surrogates are in close agreement with those of RD387 gasoline. Nevertheless, because these surrogates heavily rely on paraffins, the H/C ratio of RD387 is not reproduced (H/C ratio of surrogates is 1.974 and 2.053, respectively, while it is 1.85 for RD387).

As the RON and MON of RD387 are not known, the methodology for surrogate composition definition is rather applied considering the AKI as constraint. Since the AKI is simply the arithmetic average of the RON and MON values, such a constraint is just the arithmetic averaging of Eqs. (7) and (8). Therefore, the composition of the ternary surrogate representative of RD387 is obtained considering Eqs. (3) and (4) as well as the average of Eqs. (7) and (8) as constraints. The resulting surrogate, denoted Sur87t, is made of 17.6% of *n*-heptane by molar fraction, 43.5% of isooctane and 38.9% of toluene (18.6%, 51.7% and 29.6% of *n*-heptane, isooctane and toluene by volume fraction, respectively).

Because a direct experimental comparison of Sur87t, Gauthier's surrogates and RD387 within a shock tube was not possible for the present paper, numerical comparisons are performed with the Chemkin solver. For this purpose, the TRF detailed kinetics scheme of Anderlohr et al. [11] is used. Conditions from [8] are computed for Sur87t, Gauthier A and B. Fig. 2 indicates that auto-ignition delays for Sur87t closely match those of both Gauthier's surrogates.

The comparison at stoichiometry between numerical auto-ignition delays for surrogates (Sur87t and Gauthier A) and experimental measurements from [8] confirms that Sur87t provides similar auto-ignition delays to those of Gauthier's surrogate and by transitivity to those of gasoline (Fig. 3). The numerical auto-ignition delays for surrogate Gauthier A appear to be slightly longer than the experimental ones, due to the computation method and discrepancies of the detailed mechanism. Nevertheless, Fig. 3 clearly shows that surrogates Gauthier A and Sur87t are equivalent from the auto-ignition point of view.



Fig. 2. Comparison of computed surrogate auto-ignition delays (Sur87t, Gauthier A and B). Constant-volume Chemkin computations with the TRF detailed chemistry scheme of Anderlohr et al. [11] for conditions from [8]. Dashed line indicates equal auto-ignition delays for Gauthier A or B and Sur87t.

These results confirm that the methodology is able to provide surrogates with the same auto-ignition behaviour as other already published surrogates that have been validated in shock tube for auto-ignition delay. The added value of Sur87t with respect to Gauthier's surrogates is the reproduction of the H/C ratio of RD387, which is capital for engine modelling purpose.

5.2. Validation based on engine data

The proposed methodology aims to define surrogates for gasoline emulation under auto-igniting conditions in engines. Therefore, the best possible validation is a direct experimental comparison of gasoline and its surrogate on a kinetically-driven operating point in an engine. To do so, ULG95 and Sur95t (Table 2) are supplied to an engine operated in Controlled Auto-Ignition (CAI) combustion mode with the Negative Valve Overlap strategy.

CAI is a low-temperature combustion mode that relies on the auto-ignition of a gasoline/air mixture highly-diluted with hot burnt gases to ensure high efficiency and low pollutant emissions [2,32]. In Port Fuel Injection (PFI) engines, such a combustion mode purely relies on premixed auto-ignition without any diffusion effect or flame propagation [7]. The lack of flame propagation

ensures a better validation of the surrogate than with a knocking operating point since it is not sure that a surrogate built for auto-ignition has a similar flame propagation to that of gasoline.

The experiments were carried out on a PFI single-cylinder research engine equipped with a fully Variable Valve Actuation device [32] (see details about the engine in Table 4). The experimental conditions are a rotational speed of 2500 RPM and an Indicate Mean Effective Pressure (IMEP) of 160 kPa, obtained for a stoichiometric mixture (see additional details on the operating point in Table 5). Tests have been conducted on other operating points and have shown similar trends (not shown here).

These engine tests have been performed with the French unleaded gasoline available at that time, not for all samples from the 2005–2009 period. Therefore, to check that the gasoline sample has no major influence on the engine results, an additional repeatability test on a large number of samples has been conducted and results are detailed in Appendix B.

Fig. 4 depicts the experimental in-cylinder pressure traces for both ULG95 and Sur95t on the same operating point (identical loads, intake pressures and air mass flow rates). The pressure evolutions at the end of the compression are identical, which confirms that the change in fuel does not induce a change in trapped mass or in in-cylinder thermodynamic conditions. Since the air mass flow rate is identical for both fuels, the identical trapped mass implies an identical trapped burnt gas mass or dilution rate. With these identical in-cylinder conditions during compression, combustion phasing is similar for both fuels with a slightly slower heat release for Sur95t. This result confirms that Sur95t behaves similarly to ULG95.

In addition to the combustion phasing and speed, Sur95t also provides similar engine-out emissions to those of ULG95, which is a key feature of the surrogates defined according to the proposed methodology. The indicated engine-out unburned hydrocarbons (uHC), CO and CO₂ emissions for Sur95t and ULG95 are detailed in Table 5. The greenhouse gas emissions (CO₂) are within less than a percent, while the CO emissions are about 4% lower for the gasoline than for the surrogate and the discrepancy about uHC emissions is about 10%. The very similar exhaust temperatures is a further confirmation of the proximity of the lower heating values of both fuels.

This result confirms that the methodology is able to provide surrogates for gasoline that are representative for auto-ignition phenomena, for carbon-containing pollutant emissions and for the amount of released energy. Such a representative surrogate is now introduced in a CFD code to numerically emulate gasoline.



Fig. 3. Comparison at stoichiometry of (left) experimental auto-ignition delays of gasoline RD387 and surrogate Gauthier A (data from [8]) and of (right) numerical auto-ignition delays of surrogates Sur87t and Gauthier A (constant-volume Chemkin computations using the detailed chemistry scheme from [11]).

Table 4	
Main engine	characteristics.

Table 4

Engine type	Single-cylinder
Injection system	Port fuel injection
Combustion mode	Controlled Auto-Ignition
Trapping strategy	Negative valve overlap
Bore	82.7 mm
Stroke	93 mm
Connecting rod length	144 mm
Compression ratio	12.0:1

Table 5

Experimental operating conditions and pollutant emissions.

	ULG95	Sur95t
Engine speed	2500 RPM	2500 RPM
IMEP	160 kPa	160 kPa
Fuel/air eq. ratio	1.0	1.0
Intake pressure	91.4 kPa	92.8 kPa
Air flow rate	6.63 kg/h	6.60 kg/h
Exhaust temperature	530 K	541 K
Unburned hydrocarbon emissions	7.5 g/kW h	8.2 g/kW h
Carbon monoxide emissions	21.2 g/kW h	21.9 g/kW h
Carbon dioxide emissions	829.3 g/kW h	832.1 g/kW h



Fig. 4. In-cylinder pressure traces obtained for ULG95 and Sur95t at a rotational speed of 2500 RPM and a load of 160 kPa IMEP (Controlled Auto-Ignition combustion mode).

6. Use of a ternary surrogate for gasoline emulation within a 3D CFD code

The ultimate objective of surrogate definition is not to perform engine tests with such a compound mixture but to emulate gasoline behaviour during engine modelling. Therefore, in the present section, the proposed surrogate Sur95t is used as input for the 3D CFD modelling of the CAI operating point defined in Section 5.2 in order to fully validate the approach.

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6.1. Numerical tools

3D CFD computations are performed with a RANS (Reynolds Averaged Navier–Stokes) code developed at IFPEN [33] using a finite volume method on unstructured and conformal hexahedral meshes and a $k - \epsilon$ RNG turbulence model. For PFI CAI engines, purely premixed combustion of a mixture with few heterogeneities occurs [7]. Consequently, combustion modelling is performed with a simple burnt/unburned gas conditioning in each cell. The tabulation approach called TKI [34] is selected for chemistry description.

The TKI model [34] provides fuel auto-ignition delays and a description of the consequent heat release, deduced from detailed chemistry calculations performed prior to the CFD simulation. The TKI look-up tables are a collection of constant-pressure auto-igniting reactors stored for all conditions embraced in engines. The stored quantities are then read during the 3D CFD simulation depending on the local in-cell conditions. The table input parameters are the fresh gas temperature, pressure, fuel/air equivalence ratio and dilution rate.

The TKI model has already been successfully applied to the modelling of a PFI CAI engine operated with PRF 65 [35,36]. In order to model an engine operated with ULG95, Sur95t composition (see Table 2) is used to build the TKI tables with the detailed chemistry mechanism from [11].

Because CAI operation relies on burnt gas trapping with specific exhaust valve lift profiles, computation starts at exhaust valve opening. Exhaust, intake and compression strokes are successively simulated to precisely describe the mixture stratification and the thermal state near combustion Top Dead Center. Meshes extend towards the intake and exhaust sides as far as the inlet and outlet crank-resolved pressure sensors in order to use their measurements as boundary conditions.

6.2. Numerical results

Fig. 4 compares the numerical in-cylinder pressure trace obtained with Sur95t as input with the experimental measurements for ULG95. First, it is noteworthy that in-cylinder conditions prior to auto-ignition are identical for the numerical results and the experimental measurements. Indeed, the numerical air mass flow rate, the averaged intake pressure and the in-cylinder pressure trace simultaneously match the experiment which ensures that in-cylinder temperature and dilution rate are accurate.

Fig. 4 also shows that the auto-ignition timing is correctly predicted by the CFD approach. The certainty to obtain such a result for the right in-cylinder conditions validates the approach in terms of gasoline auto-ignition timing prediction. Despite the right autoignition timing, the heat release rate is not perfectly described: the in-cylinder pressure trace during combustion lies between the experimental evolutions for Sur95t and ULG95. Nevertheless, the difference between both is restricted.

Eventually, the pressure evolution during expansion confirms that the energy content in Sur95t is also a close match to that of gasoline. Consequently, these calculation results illustrate that the modelling approach is relevant: Sur95t is an accurate surrogate

Table 6

Compound properties used for computations in the present paper. Properties are from [15,20].

	RON	MON	Molar weight (g/mol)	Density at 298 K (kg/m ³)	Lower heating value (kJ/kg)
n-Heptane	0.0	0.0	100.2	684	44566
Isooctane	100.0	100.0	114.2	692	44310
Cyclohexane	83.0	77.2	84.2	779	43450
Toluene	120.0	103.5	92.1	867	40589
Cyclohexene	83.9	63.0	82.1	811	42886
Ethanol	130.0	103.0	46.1	792	26800

Fig. 5. Composition of mixtures of toluene, isooctane and *n*-heptane having a RON of 95, as predicted by the correlations of Morgan et al. [10] (Eq. (A.2)) and of Ghosh et al. [37] (Eq. (A.3)) as well as by Eq. (A.4). For each toluene volume fraction, the hollow symbol provides the volume fraction of *n*-heptane and the solid symbol the isooctane content.



Fig. 6. Sensitivity of mixtures of toluene, isooctane and *n*-heptane having a RON of 95, as predicted by the correlations of Morgan et al. [10] (Eq. (A.2)) and of Ghosh et al. [37] (Eq. (A.3)) as well as by Eq. (A.4). Corresponding compositions are depicted in Fig. 5.



Fig. 7. Repeatability test on a Controlled Auto-Ignition operating point over multiple days and gasoline samples from the 2005–2009 period.

for ULG95 since it behaves like gasoline during engine tests and can be successfully used to predict auto-ignition with CFD using its detailed chemistry.

7. Conclusion

A methodology using simple gasoline properties has been proposed to define proportions of compounds in gasoline surrogates dedicated to auto-ignition in engines. The resulting surrogates not only behave similarly to gasoline from the auto-ignition point of view but also have identical atomic content leading to similar density and lower heating value, which are key parameters for engine operation.

A mixture of only three well-chosen compounds appears to already be a proper gasoline surrogate if proportions are chosen according to the methodology. Experimental engine results show that the auto-ignition timing but also the power output and the pollutant emissions can be recovered on a CAI operating point. 3D CFD results on this validation operating point indicate that the final aim of gasoline emulation in engine codes with such a surrogate can be successfully reached.

The inclusion of more compounds leads to a convergence towards more gasoline properties as well as a reproduction of the classification of gasoline compounds into chemical families. This last item will be of utmost importance when late timing direct injection SI or CAI operating points will be considered since soot emissions will be a major limitation.

The basics of the present methodology may be accomodated to other types of fuel. For instance, Diesel surrogate composition would be computed replacing the Octane Number by the Cetane Number.

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Appendix A. Computation of Research and Motor Octane Numbers of mixtures of fuels

Formulating an expression for the Octane Number of mixture of fuels is not so easy because Octane Numbers (ON) are not strictly additive properties when computed based on the compound volume fractions v_t [10,15,37]. The non-linear link between compound ON and mixture ON is due to the chemical interactions between the intermediate species from each compound during the pre-ignition reactions. To account for the deviation from linearity, several authors have proposed expressions including corrections [10,15,37].

Morgan et al. [10] have measured the ON of various mixtures of *n*-heptane, isooctane and toluene and have compared the experimental data with the computation results from different models. They have shown that the linear combination of compound ON weighted by the volume fraction is not an accurate model to represent the mixture ON (*ON_{mix}*):

$$ON_{mix} \neq \sum_{i=1}^{n} v_i ON_i \tag{A.1}$$

where ON_i is the Octane Number of species i.

Morgan et al. [10] have proposed two alternative methods for calculating TRF mixture ON: a second order model based on compound volume fractions and a modified linear by volume model.



Despite a simpler formulation, the modified linear by volume model appears to be the most accurate. The non-linear behaviour is reproduced through a coupling term between PRF and toluene volume fractions and a second order term for toluene volume fraction:

$$ON_{mix} = ON_{iC_8H_{18}}p + a_1 v_{C_7H_8} + a_2 v_{C_7H_8}^2 + a_3 p v_{C_7H_8}$$
(A.2)

where $p = \frac{v_{iC_8H_{18}}}{v_{iC_8H_{18}} + v_{nC_7H_{16}}}$ is the fraction of isooctane in the PRF part of the mixture, while a_1 , a_2 and a_3 are fitted constants (see values in [10]).

Ghosh et al. [37] have analysed a large number of fuel mixtures, not necessarily limited to TRFs, and have identified a global dependence on the chemical family of each compound for the computation of the mixture ON. They have proposed a model based on a linear weighting by the compound volume fractions multiplied by constants defined for each chemical family. When olefins or naphthenes are included in the mixture an additional interaction term is added. For TRF mixtures, the relation for ON computation is:

$$ON_{mix} = \frac{\sum_{i=1}^{n} v_i \beta_i ON_i}{\sum_{i=1}^{n} v_i \beta_i}$$
(A.3)

where β_i are the constants depending on the chemical family of the compound (see values in [37]).

An alternative model for the computation of TRF mixture ON is proposed here. It is based on a linear averaging weighted by compound molar fractions rather than volume fractions:

$$ON_{mix} = \sum_{i=1}^{n} x_i ON_i \tag{A.4}$$

where x_i is the molar fraction of species *i*. Octane Numbers of pure compounds considered to calculate surrogate compositions with Eq. (A.4) during the present study are summarised in Table 6.

Despite its quite simple form, Eq. (A.4) provides results similar to those of the correlations of Morgan et al. [10] and Ghosh et al. [37], as depicted in Figs. 5 and 6. Fig. 5 shows the composition of all mixtures of toluene, isooctane and *n*-heptane having a RON of 95, according to the correlations of Morgan et al. [10] and of Ghosh et al. [37] as well as Eq. (A.4). The proposed correlation (Eq. (A.4)) closely matches the results from the other two correlations, especially when the constraint from EN 228 specification about aromatic content in gasoline (<35 vol%) is respected. Fig. 6 depicts the sensitivity (S = RON - MON) of the same mixtures as predicted by the correlations of Morgan et al. [10] and of Ghosh et al. [37] as well as by Eq. (A.4). Again, Eq. (A.4) provides results that are very similar to those of the correlation of Morgan et al. [10]. The results of Ghosh et al. [37] are notably different but not really trustworthy since a clearly negative sensitivity is predicted for PRFs (toluene fraction = 0), while it should be zero by definition.

Appendix B. Influence of gasoline sample on engine operation

Combustion evolutions of gasoline ULG95 and its surrogate (Sur95t) are compared in Section 5.2 to validate the behaviour of the surrogate. This comparison is necessarily performed with a unique gasoline sample. Therefore, the question of the representativity of this sample with respect to the full range of fuels from the 2005–2009 period may be raised.

In order to verify the repeatability of the measurements over time and the lack of heavy dependence on the gasoline sample, a unique operating point has been measured over a wide number of days for various gasoline samples from the 2005–2009 period. This operating point has been measured on the same engine (Table 4) as that in Section 5.2 but the engine load is 200 kPa IMEP and the engine speed is 2000 RPM. Results for measurements over 50 days are gathered into Fig. 7 for IMEP and peak pressure angle timing. These results show that the dispersion from day to day for a unique gasoline sample are larger than the differences observed when the gasoline sample is changed. Therefore, the use of a gasoline sample rather than another does not appear as a parameter capable of changing the conclusions about surrogate validation.

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Review

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Recent progress in the development of diesel surrogate fuels

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ABSTRACT

There has been much recent progress in the area of surrogate fuels for diesel. In the last few years, experiments and modeling have been performed on higher molecular weight components of relevance to diesel fuel such as n-hexadecane (n-cetane) and 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane). Chemical kinetic models have been developed for all the n-alkanes up to 16 carbon atoms. Also, there has been experimental and modeling work on lower molecular weight surrogate components such as n-decane and n-dodecane that are most relevant to jet fuel surrogates, but are also relevant to diesel surrogates where simulation of the full boiling point range is desired. For two-ring compounds, experimental work on decalin and tetralin recently has been published. For esters, kinetic mechanisms for compounds of lower molecular weights but similar to those found in typical biodiesel blendstocks also have been published. For multi-component surrogate fuel mixtures, recent work on modeling of these mixtures and comparisons to real diesel fuel is reviewed. Detailed chemical kinetic models for surrogate fuels are very large in size, so it is noteworthy that significant progress also has been made in improving the mechanism reduction tools that are needed to make these large models practicable in multidimensional reacting flow simulations of diesel combustion. Nevertheless, major research gaps remain. In the case of iso-alkanes, there are experiments and modeling work on only one of relevance to diesel: iso-cetane. Also, the iso-alkanes in diesel are lightly branched and no detailed chemical kinetic models or experimental investigations are available for such compounds. More components are needed to fill out the iso-alkane boiling point range. For the aromatic class of compounds, there has been little work for compounds in the boiling point range of diesel. Most of the new work has been on alkyl aromatics that are of the range C7-C9, below the C10-C20 range that is needed. For the chemical classes of cycloalkanes and esters, experiments and modeling on higher molecular weight components are warranted. Finally for multi-component surrogates needed to treat real diesel, the inclusion of higher molecular weight components is needed in models and experimental investigations.

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1. Introduction

Detailed chemical kinetic models are important because they help enable the computational design and optimization of practical devices such as internal combustion engines by enabling simulation of the combustion of transportation fuels like gasoline, diesel, and jet fuels. Development of detailed chemical kinetic models is challenging. Gasoline, diesel and jet fuels derived from conventional petroleum sources are composed of hundreds to thousands of compounds. Development of models that represent all these components is prohibitive because the model would be too large for current computational resources. Also, all the fundamental data needed for development of such a model (e.g., chemical kinetic rate constants, reaction paths, thermodynamic parameters) are not available. Thus, simplified "surrogate fuels" are useful for representing current transportation fuels. A surrogate fuel is defined as a fuel composed of a small number of pure compounds whose behavior matches certain characteristics of a target fuel that contains many compounds (e.g., a market diesel fuel). Both the chemical and physical characteristics of the target fuel need to be represented by the surrogate fuel so that the surrogate will properly reproduce not only the combustion characteristics of the fuel, but also the injection, vaporization, and mixing processes that precede ignition in practical devices. Relevant chemical characteristics of the fuel may include ignition behavior, molecular structures, adiabatic flame temperature, C/H/O content, and sooting propensity. Relevant physical characteristics may include volatility parameters, density, viscosity, surface tension, and diffusion coefficients.

In addition to enabling accurate computational simulations, surrogate fuels are also useful experimentally. First, experimental data on surrogate fuels are needed to validate surrogate fuel models. Second, it is useful to develop surrogate fuels to provide standardized fuels whose compositions do not change over time. These standardized fuels can be used so that experiments are reproducible. They also allow testing of the same fuel in different experimental devices, geographic locations and using different analysis techniques so that comparisons can be made without fuel variability complicating interpretation of the results. The compositions of gasoline, diesel and jet fuels vary as the refinery streams and/or other blendstocks from which they are derived change with time. Even if standardized fuels are blended from refinery streams and stored for later use, there is only a finite volume of these standardized fuels available, and they could chemically deteriorate over time. In contrast, standardized fuels from surrogate components can be reformulated at any time from their constituent pure compounds. Finally, the study of surrogate fuels focuses attention on the fuel properties that are most important for determining engine efficiency, emissions, and other critical performance characteristics. In deciding which properties should be matched between the surrogate and the target fuel, the researcher incorporates hypotheses about the effects of specific fuel properties on in-cylinder mixing and combustion processes. If the resultant surrogate fuel fails to match the performance of the target fuel adequately, these underlying hypotheses must be reassessed and refined, ultimately leading to an improved understanding of the fundamental relationships between fuel properties and engine performance.

The development of a surrogate fuel model is a lengthy process [1–5]. Chemical kinetic models for each of the pure compounds in the surrogate fuel must be developed and validated by comparison to experimental data. A procedure needs to be identified to choose the relative concentration of each component in the surrogate to best reproduce the properties of the target fuel. The chemical kinetic mechanisms of the individual components need to be combined and important cross reactions between mechanisms included. The surrogate fuel model needs to be reduced in size so that it can be used in multi-dimensional computational fluid dynamics (CFD) models for simulating engine combustion. Finally, the surrogate fuel model needs to be validated by comparison with surrogate- and target fuel experiments in practical combustion devices of interest.

Physical property models need to be developed for surrogate fuel components and their mixtures. These include models for density, volatility, surface tension, viscosity, thermal conductivity and species transport of the components and their mixtures. Measurements of these properties are also needed for validation of the model. These properties are needed to predict properly the fuel spray break-up, evaporation, and species transport that determine the reacting mixture temperature and species concentration fields.

In this paper, the current status of diesel fuel surrogate development will be assessed. The review will build on previous reviews of experimental and chemical kinetic modeling of hydrocarbon fuels. In 2003, Simmie [6] reviewed the status of chemical kinetic models and experimental data for the oxidation of hydrocarbon fuels from each of the chemical classes (n-alkanes, iso-alkanes, cycloalkanes, alkenes and aromatics). The progress towards the development of surrogate fuels for diesel was reviewed in the 2007 Farrell et al. paper [1]. Battin-Leclerc [7] recently reviewed in depth the progress in the development of detailed chemical kinetic mechanisms for gasoline and diesel surrogate fuels. The reader is referred to these excellent reviews for relevant work done prior to 2008. The current paper will focus on research progress from 2008 to the present, except for earlier studies that are relevant but have been omitted in previous reviews. In the current review, the status of chemical kinetic models and experimental validation data of surrogate fuel components and their mixtures will be assessed. Next, chemical kinetic model reduction will be discussed, followed by an examination of progress toward models and measurements of physical properties of surrogate fuels. The paper concludes with recommendations for future work and a summary.

2. Chemical kinetic models for diesel fuel components

The relevant components for diesel fuel surrogates have been previously discussed and identified in [1], but they will be reviewed here and expanded to include biodiesel blending streams. The primary chemical classes of the components in petroleum-based diesel fuel are n-alkanes, iso-alkanes, cycloalkanes and aromatics (Fig. 1). Although the composition of petroleum-based diesel fuel is highly variable, there are some trends [1]: The carbon numbers of the components range from approximately C10–C22. An average carbon number is 14 or 15. The iso-alkanes are usually lightly branched with one or two side methyl groups. The cycloalkanes typically have one ring with multiple alkyl side chains. There are

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Fig. 1. Relative amounts of various chemical classes in diesel fuel and possible compounds to represent these chemical classes in a diesel surrogate fuel.

some two-ring cycloalkanes with alkyl side chains as well. The aromatics are usually one ring with multiple side chains. The average carbon number of the aromatics is about C12 as shown in the composition data in [1]. This carbon number is lower than the other chemical classes. There are also some two-ring aromatics with alkyl side chains.

Since the publication of [1], bio-derived blending streams for diesel have become increasingly important. One such blending stream is "renewable diesel", which is produced by hydrotreating bio-derived oils or fats in a refinery (e.g., [8,9]). Although detailed compositional information for renewable diesel does not appear to be available in the literature, renewable diesel is likely primarily comprised of n-alkanes and iso-alkanes, with the iso-alkanes resulting from isomerization approaches applied in the refinery to improve the cold-flow performance of the fuel (see bottom of p. 84/ top of p. 85 of [10] and [9]). Another important bio-derived blending stream is biodiesel. Biodiesel is defined as a "fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats" [11]. While petroleum-based diesel may contain thousands of compounds, biodiesel fuels typically contain fewer than ten. Fig. 2 shows the single C17 and four C19 methyl esters primarily comprising biodiesel fuels produced from soy and rapeseed [12,13].

In the following sections, recent developments in chemical kinetic models and experiments for each chemical class will be discussed in turn.

2.1. n-Alkanes

There has been much recent progress on the development of chemical kinetic models for components relevant to diesel fuel. Most of the progress has been in the chemical class of n-alkanes. Chemical kinetic detailed mechanisms for n-alkanes from n-C8 up to n-C16 have been developed [15,16]. Together with previous work [17,18], this allows the simulation of all n-alkanes up to C16. The mechanisms include low temperature chemistry, which is essential for investigating low temperature combustion strategies in diesel engines. Fig. 3 shows a simulation of the ignition delay of large n-alkanes at 13 bar from low to high temperature [15]. The model predicts that all n-alkanes from n-C7 to n-C16 ignite with nearly the same ignition delay times within a factor of about 1.5. This trend was not seen in the simulations of [16], but was seen in the shock tube experiments of [19] discussed later. For C10 and C12 n-alkanes, there has been considerable progress reported in the literature. You

et al. [20] developed a mechanism for n-dodecane and n-decane that is valid above 850 K. It was validated by comparison to pyrolysis experiments in plug flow and jet stirred reactors, and by comparison to shock tube ignition delay times and laminar flame speeds. This model has been further improved and validated, and is available at [21]. In other work, Zhang et al. [22–25] extended a high temperature, n-heptane mechanism up to n-hexadecane with a focus on predicting the formation of the unsaturated soot precursor species in premixed flames.

There also has been considerable progress in acquiring experimental data for large n-alkanes. These experimental data are valuable for validating detailed chemical kinetic mechanisms and for gaining insight into the behavior of these fuels. Shen et al. [19] have recently obtained shock tube ignition data for a series of large



Fig. 2. Molecular structures, names, chemical formulas, and Chemical Abstracts Service (CAS) numbers of the five primary methyl esters found in biodiesel fuels produced from soy and rapeseed. Molecular structures are from [14].



Fig. 3. Ignition behavior of a series of large n-alkanes (stoichiometric fuel-air mixtures, initial pressure of 13.5 bar, temperatures from 650 to 1200 K) [15].

n-alkanes up to C16. Their experiments were performed over a temperature range of 786–1396 K, a pressure range of 9–58 atm and for equivalence ratios of 0.25, 0.5, and 1.0. These conditions of pressure and temperature simulate conditions found in internal combustion engines. Experimental results in Fig. 4 show that the measured ignition delay times are very similar for a series of large n-alkanes. The curves that encompass the data give about a factor of two variation in ignition delay times compared to a factor of 1.5 seen in the Westbrook et al. simulations (Fig. 3) and indicate a general trend for large n-alkanes. However, the experimental work does not cover the complete low temperature regime from 650 to 780 K. In other work, Biet et al. [16] obtained experimental data for n-decane and an n-hexadecane/n-decane mixture in a jet stirred reactor at 1 atm over a range of temperatures from 550 to 1100 K. Their detailed chemical kinetic model was able to reasonably reproduce their experimental data. In a subsequent paper on the same fuel mixture, Hakka et al. [26] were able to identify a much more complete spectrum of intermediate species including high molecular weight alkenes, aldehydes, ketones and cyclic ethers in the jet stirred reactor.

Significant experimental validation data recently have become available in the lower molecular weight range of diesel (C10 and C12 n-alkanes) because this carbon range is also important for jet surrogate fuels, which have received considerable recent attention. Vasu et al. [27] measured shock tube ignition delay times and OH concentration histories for n-dodecane. Their experiments were performed over a temperature range of 727–1422 K, a pressure range of 15–34 atm and for equivalence ratios of 0.5 and 1.0. Their experimental data for ignition delay times agree quite well with Shen et al. [19].

The shock tube studies above considered equivalence ratios up to 1. There is a need to investigate equivalence ratios greater than 1.0 because diesel engine ignition occurs at equivalence ratios of about 2–4 under conventional diesel engine conditions [28]. This equivalence ratio range should be extended to the low end (about $\phi = 0.3$) to explore new strategies of low temperature combustion in a diesel engine [29,30]. Thus, a range of equivalence ratios from approximately 0.3–4 is needed for fundamental validation data relevant to diesel engine conditions. Such fuelrich conditions may be challenging in a heated shock tube where adequate vaporization is difficult to achieve with high molecular weight fuels.

Davidson et al. [31] examined n-dodecane in their aerosol shock tube, which allows the investigation of ignition of high boiling point fuels without heating the shock tube. Although their experiments were at lower pressures (5.8–6.7 atm) than other studies, they found similar trends for ignition delay with temperature as Vasu et al. when the usual P^{-1} pressure dependence was assumed. Zhukov et al. [32] examined the shock tube ignition of n-decane at high pressures up to 80 atm and temperatures ranging from 800 to 1300 K for stoichiometric and lean mixtures. The above experimental data were all taken at conditions relevant to internal combustion engines.

Kumar et al. [33] studied the ignition of n-decane in a rapid compression machine (RCM) at compressed gas pressures of 7–30 bar, compressed gas temperatures of 635–770 K and equivalence ratios of 0.5–2.2. They found two-stage ignition behavior over the entire range of conditions that they investigated. Their measured ignition delay times agree with the shock tube ignition delay measurements of Pfahl et al. [34] at an equivalence ratio of 0.5, but are shorter than Pfahl et al. [34] at near stoichiometric conditions. Discrepancies were identified between Kumar et al's measured ignition delay times and the predictions of two chemical kinetic models [15,35]. Kumar et al. [36] also measured the laminar flame speeds of n-decane and n-dodecane in a counterflow configuration at unburned reactant temperatures of 360–470 K,



Fig. 4. Experimentally measured ignition delay times for C7, C10, C12 and C14 n-alkanes at an equivalence ratio of 0.5 [19]. Reprinted ("Adapted" or "in part") with permission from [19]. Copyright 2009 American Chemical Society.

equivalence ratio range of 0.7-1.4 and atmospheric conditions. Biet et al. [16] improved the automatic generation of a chemical kinetic mechanism for n-alkanes by improving the treatment of the consumption of primary products such as alkenes, aldehydes and cyclic ethers. They applied the mechanism to the simulation of their new experimental data for stoichiometric mixtures of n-decane and n-decane/n-hexadecane in a jet stirred reactor at 1 atm over a temperature range of 550-1100 K. They also used the new chemical kinetic mechanism to simulate the experimental data of n-decane in a perfectly-stirred reactor by Dagaut et al. [37] and n-dodecane in a flow reactor [38]. The agreement between the new chemical kinetic mechanism and measurements for the different experimental configurations and n-alkanes was reasonable. In a later study, Hakka et al. [26] measured a more complete set of intermediate products for n-decane and an n-decane/n-hexadecane mixture in a jet stirred reactor at the same conditions. A summary of experimental studies on n-decane performed prior to 2007 can be found in Dagaut and Cathonnet [39].

For n-alkanes, more experimental data are needed to fill out the carbon range from C15 to C20. This is a challenge because it is difficult keep these higher molecular weight fuels in the vapor phase in fundamental experimental devices such as shock tubes. Nevertheless, more experimental data are now available for large n-alkanes, and these additional data should be used to help further validate and develop chemical kinetic models. An additional need is for experimental validation data that include species typical in engines when exhaust gas recirculation (EGR) is employed. These species are water, carbon dioxide, carbon monoxide, nitric oxide, molecular nitrogen and others. A recent paper [40] has identified discrepancies between chemical kinetic model predictions and experimental measurements when EGR is included. The work focused on the effects of the EGR species water, carbon dioxide, and molecular nitrogen.

2.2. iso-Alkanes

There has been significant progress in the area of iso-alkanes, particularly for iso-cetane (2,2,4,4,6,8,8-heptamethylnonane). Isocetane has 7 methyl branches, while most iso-alkanes in diesel fuel contain one or two methyl branches [1]. The effect of these additional methyl branches likely is reflected in the low cetane number of iso-cetane of 15 [41]. Iso-cetane has an assigned cetane number because it is a primary reference fuel for diesel. Primary reference fuels are used to rate diesel ignition properties through the cetane number test [42]. A low cetane number means a fuel component is relatively resistant to ignition in a diesel engine while a high cetane number indicates it is easily ignited. Compared to isocetane, lightly branched iso-alkanes like 7,8-dimethyltetradecane and 9-methylheptadecane are more easily ignitable and have cetane numbers of 40 and 66, respectively [43]. Although isocetane's ignition properties are not representative of lightly branched iso-alkanes, its low reactivity can be used to balance high reactivity components, like n-alkanes, in a diesel surrogate. Because of its use as a primary reference fuel, iso-cetane is readily available to experimentalists in high purity at relatively low cost. It is also an iso-alkane that is in the middle of the carbon range for diesel fuel, C10-C22, a feature which helps in matching the distillation curve of diesel.

Oehlschlaeger et al. [44] measured shock tube ignition delay times for iso-cetane at conditions relevant to diesel engines (temperatures from 953 to 1347 K, pressures from 8 to 47 atm and for equivalence ratios of 0.5, 1.0 and 1.5). These measurements were compared to a newly developed chemical kinetic mechanism for iso-cetane based on a previous and successful model for iso-octane [45]. The computed and measured results showed good agreement. A similarity was found between the autoignition process of isocetane and iso-octane. The low reactivity of both fuels at these intermediate to high temperatures can be attributed to the production of iso-butene which produces relatively stable 2-methyl-allyl radicals.

Dagaut et al. [46] investigated the oxidation of iso-cetane/O2/N2 mixtures in a jet stirred reactor at 10 atm and equivalence ratios of 0.5, 1.0 and 1.5. They measured the species concentrations in the reactor over a temperature range from 770 to 1070 K. Their results showed iso-butene as the major hydrocarbon intermediate. They simulated their results with two chemical kinetic models. One had lumped chemistry for the whole scheme [47]. The other used automatic generation to produce the mechanism [48] which had detailed chemistry for the fuel, CO and C1 species, with lumped chemistry for the remaining reactions. Neither detailed model included low temperature chemistry since none was observed with the highly-diluted mixtures used. The fully lumped model [47] was unable to satisfactorily reproduce the experimental data. The partially lumped model [48] simulated the fuel profiles very well, but predicted ethene instead of iso-butene as the major hydrocarbon intermediate.

Recently, Ranzi et al. [49] corrected the erroneous computed results reported in [46] that showed poor agreement of the lumped iso-cetane model compared to the stirred reactor experiments of iso-cetane [46]. They stated that the simulation error was due to convergence problems. Once the simulations were corrected, the agreement between the Ranzi model predictions and the stirred reactor measurements was reasonable.

There is still a considerable gap in knowledge for large isoalkanes, particularly lightly branched iso-alkanes that are more representative of diesel fuel components. Inclusion of these additional iso-alkanes would enable the development of a surrogate palette that more accurately captures the structure and properties of the iso-alkanes in market diesel fuels. With regard to physical properties, experimental and modeling characterization of a series of iso-alkanes may be helpful to properly represent the distillation curve of diesel fuel. Huber et al. [50] have found that iso-alkanes need to be included in a surrogate to properly simulate the thermal conductivity of liquid diesel fuel.

2.3. Cycloalkanes

Cycloalkanes may comprise one-third or more by weight of diesel fuels, depending on crude source and degree of hydroprocessing (see Table 1 and Fig. 2 of [1] as well as [51]). Cycloalkanes are much higher in alternative diesel fuel derived from oil sands deposits [51]. The cycloalkanes in diesel usually have multiple, alkyl side chains [1]. Discussed below is recent progress in chemical kinetic models and experimental data, starting with C6 cycloalkanes and increasing in carbon number.

There has been considerable progress on the development of chemical kinetic models for cyclohexane. Detailed chemical kinetic models for the oxidation of cyclohexane have been developed [52–54]. These models generally reproduce well the oxidation of cyclohexane under conditions in a stirred reactor and rapid compression machines [55,56]. In other work, Zhang et al. [57] developed a chemical kinetic model for cyclohexane and compared their model predictions to experimentally measured intermediate products in a low-pressure, premixed flame [58]. They focused on the pathways that lead to benzene formation.

Recently, a more accurate description of important low temperature reactions for cyclohexane oxidation has become available [59]. These reactions involve the addition of molecular oxygen to cyclohexyl radicals and subsequent isomerization reactions including the temperature and pressure dependence of their rate constants. This new knowledge of the complex behavior of these rate constants will likely allow a more accurate description of the ignition behavior of cyclohexane over the wide temperature and pressure range found in a diesel engine.

Much new experimental data on cyclohexanes has recently become available. Mittal and Sung [60] investigated the ignition of methylcyclohexane in an RCM at equivalence ratios of 0.5, 1.0 and 1.5, pressures of 15 and 25 bar and over a compressed gas temperature range of 680-905 K. The chemical kinetic model of Pitz at al. [61] predicted the shape of the measured ignition times with temperature, but the predicted times were longer than the measured times (Fig. 5). A two-stage ignition with a strong negative coefficient behavior was observed where the ignition delay increases with increasing temperature. Yang and Boehman [62] have studied the oxidation of cyclohexane and methylcyclohexane under motored engine conditions. They measured the concentration of intermediate products including cyclic ethers that are an indication of low temperature chemistry. They showed that a methyl group side chain on the ring (i.e., methylcyclohexane) enhances the reactivity of the fuel. Vasu et al. [63,64] measured the ignition delay times of methylcyclohexane over a wide range of temperature and pressure (800–1550 K, 1–50 atm, and $\phi = 0.5 - 2.0$). They also measured OH concentration histories to provide further validation targets for chemical kinetic models. Daley et al. [65] investigated the shock tube ignition of cyclohexane



Fig. 5. Comparison of experimental (symbols) and computed (lines) ignition delays of methylcyclohexane for (a) compressed gas pressure, $P_C = 25.5$ bar, Mix #1 ($O_2/N_2/Ar = 10.5/12.25/71.75$, $\phi = 1.0$) and (b) $P_C = 15.1$ bar, Mix #2 ($O_2/N_2/Ar = 7.16/16.35/71.75$, $\phi = 0.5$). Reprinted from [60] with permission from Elsevier.

and cyclopentane over a range of conditions important for internal combustion engines (11–61 atm, 847–1379 K, and equivalence ratios of phi = 1.0, 0.5, and 0.25). They found that current models [52,53] captured the general trends of their experimental data, but their predicted ignition delays were generally longer than those measured.

Vanderover and Oehlschlaeger [66] investigated the shock tube ignition of methylcyclohexane and ethylcyclohexane over wide range of conditions (881–1319 K, 11–70 atm, $\phi = 0.25$, 0.5, 1.0). Their results showed the predicted ignition delay times from a recent chemical kinetic model [61] were too long at high pressure (50 atm). Sivaramakrishnan and Michael [67] experimentally measured rate constants for OH radicals with cyclohexane and methylcyclopentane. These rate constants will allow a more accurate description of the consumption reactions for cycloalkanes. In other work, Ciajolo et al. [68] measured the intermediate products of cyclohexane in a rich premixed flame and compared the results to their lumped chemical kinetic mechanism for cyclohexane. They found good agreement between the experimental and predicted profiles. They also added a soot model to the mechanism, but were not able to predict the early soot formation observed with cyclohexane. Bieleveld et al. [69] measured the autoignition temperatures and extinction conditions for methylcyclohexane. They found its ignition and extinction behavior to be between that of n-heptane and iso-octane.

Pousse et al. [70] performed low-pressure, premixed flame studies on a methane and n-propylcyclohexane fuel mixture. The experimentally measured species profiles in the flame were compared to computed results from a chemical kinetic mechanism for n-propylcyclohexane that they developed. They further validated the mechanism by comparing computed species histories with experimental data for n-propylcyclohexane taken in a jet stirred reactor over a temperature range of 800–1100 K, equivalence ratios of 0.5, 1.0 and 1.5 and at a pressure of 10 atm. Reasonable agreement between the computed and measured results was obtained.

For two-ring cycloalkanes, Oehlschlaeger et al. [71] measured the ignition delay times for a mixture of cis- and trans-decalin over a wide range of conditions (990-1300 K, 9-15 atm and 35-48 atm, equivalence ratios of 0.5 and 1.0). They generated a lumped mechanism for decalin that contained high temperature chemistry only. The predicted ignition delay times compared reasonably well with the measured times. Yang and Boehman [72] investigated the oxidation of decalin (mixture of 62% of trans- and 38% cis- isomers) in a CFR octane-rating engine operated under motored engine conditions. They measured products in the exhaust of the engine at an engine speed of 600 rev/min, equivalence ratio of 0.25, intake temperature of 200 °C and a compression ratio range of 4.5-12.2. Decalin exhibited significant low temperature heat release in their motored engine. It reacted to aldehydes, small alkenes and CO through low temperature paths. Decalin also dehydrogenated to form hydronaphthalenes, naphthalene and tetralin. It underwent ring opening reactions. In other work, Chae and Violi [73] computed rate constants for the decomposition of decalin using density functional theory.

Although much progress has been made on cycloalkanes, more work is needed to cover the full carbon range of cycloalkanes. Single ring compounds, (C6 and C7 cycloalkanes) have been well examined. For C8 and C9 cycloalkanes (i.e., alkyl cyclohexanes), there is one study each [66] and [74], respectively. To our knowledge, there are no data available for monocyclohexanes larger than C9. However, the full diesel range for cycloalkanes extends up to about C22 with an average of C14 or C15 [1]. Thus, there is a need to examine higher molecular weight compounds. These studies are challenging because fundamental investigations usually require maintaining these high boiling point compounds in the gas phase. Also, there is limited availability of such compounds at a reasonable price, even for relatively small quantities needed in fundamental combustion experiments.

2.4. Monoaromatics

Aromatics comprise a large fraction of diesel (about 30–35% by weight on average) [1]. Most of these aromatics are monoaromatics (compounds with 1 aromatic ring) with alkyl substitutions [1]. In the following section, developments in the chemical kinetic modeling and experimental investigation of alkyl substituted benzenes are discussed. (Benzene is not included because it is not present at any significant level in diesel fuel).

There has been much progress in the development of chemical kinetic mechanisms for the only C7 aromatic, toluene. Sakai et al. [75] made many improvements in the treatment of different reaction classes in toluene. They compared computed ignition delay times to those experimentally measured in a shock tube [76,77]. Mehl et al. [78,79] made further improvements to the Sakai et al. mechanism. They were able to simulate well the experimentally measured ignition delay times of Mittal et al. [80] in a rapid compression machine and Shen et al. in a shock tube [81]. The simulations showed that the discrepancies between ignition delay times in the shock tube and rapid compression machine could be explained by heat losses in the RCM. The Shen et al. [81] shock tube experiments covered a wide range of conditions (1021-1400 K, pressures of 10-61 atm, and equivalence ratios of 1.0, 0.5, and 0.25.) They did not observe early pressure rise during the ignition process for toluene reported by Davidson and co-workers [82,83], nor did the Mehl et al. model predict such pressure rise. Blanquart et al. [84] extended their chemical kinetic mechanism to include toluene. They obtained good agreement between predicted and measured shock tube ignition delay times at high temperature and laminar flame speeds at 1 atm.

Shen et al. [85] studied the autoignition of the C8 aromatics (ortho-xylene, meta-xylene, para-xylene and ethylbenzene) in a shock tube over a wide range of conditions relevant to diesel engines (941-1408 K, 9-45 atm, equivalence ratios of 5.0 and 1.0, and fuel-air mixtures). Ethylbenzene was found to be the most reactive followed by the less reactive xylenes, ortho, meta and para. Ignition delay times for p-xylene matched up closely with their recent toluene measurements [81]. They compared their shock tube ignition delay times with previous measurements by Gail et al. [86] and Battin-Leclerc et al. [87]. They found that the overall activation energy exhibited by their experiments at high pressure was much lower than the activation energy observed by Gail et al. and Battin-Leclerc et al. Based on chemical kinetic simulations, Shen et al. attributed this difference to consumption of xylenes by radical attack (mainly OH) at high pressure under their conditions. Under the higher temperature, more dilution conditions of the earlier studies, xylene consumption occurs by thermal decomposition reactions which are known to require high activation energies.

Gail et al. [86,88,89] investigated the oxidation of ortho-, metaand para-xylenes in a jet stirred reactor over a temperature range of 900 K—1400 K, an equivalence range of 0.5—1.5 and a pressure of 1 atm. They found the reactivity of meta- and para-xylene to be quite similar while the reactivity of ortho-xylene to be much higher in comparison. This is similar to the behavior observed by Roubaud et al. [90] in a RCM with an end-of-compression temperature of 907 K where the ignition delay times of meta- and para-xylene were similar but the ignition delay times of o-xylene were much shorter. Gail et al. [86,88,89] also developed detailed chemical kinetic mechanisms to describe the oxidation of the three xylenes. They validated their mechanism by comparing computed results to their species measurements in a jet stirred reactor and ignition delay time measurements in a shock tube. Battin-Leclerc et al. [87] also developed a chemical kinetic model to simulate the oxidation of all three xylene isomers. The predictions of their model compared well with their ignition delay time measurements in a shock tube over a temperature range of 1330–1800, a pressure range of 7–9 atm and equivalence ratios of 0.5, 1.0 and 1.5. They also compared predicted species concentrations to species measurements in a atmospheric pressure flow reactor by Emdee et al. [91] and obtained reasonable agreement for meta- and para-xylene.

Roubaud et al. [90,92] also studied C9 aromatics in a RCM at compressed gas temperatures of 600-900 K and pressures of 12-15 atm. They examined the ignition of 1,2,3-trimethyl benzene, 1,2,4-trimethyl benzene, 1,3,5-trimethyl benzene and 2-ethyl toluene in stoichiometric, O2-inert mixtures. They found that 1,2,3trimethyl benzene, 1,2,4-trimethyl benzene, and 2-ethyl-toluene ignited more easily than 1,3,5-trimethyl benzene. They attributed the easier ignition to the availability of ortho alkyl groups with their more easily transferable H-atoms in the alkylbenzylperoxy radicals formed by these C9 aromatics. These internal H-atom transfers lead to chain branching and higher reactivity. Litzinger et al. [93] studied the oxidation of iso-propyl benzene in an atmospheric flow reactor at 1000 K and 1060 K, and at equivalence ratios of 0.52, 1.0 and 1.5. They determined the ratio of the abstraction rates of benzylic hydrogen atoms to primary hydrogen atoms in iso-propyl benzene to be approximately 6-1. A detailed chemical kinetic model for 1,2,4-trimethyl benzene was developed by Bikas [94] and used by Peters and co-workers [95,96] as a component in a kerosene surrogate fuel. Trimethylbenzenes also were studied in other work in binary mixtures with 1-methylnapththalene discussed below.

For C10 aromatics, Pousse et al. [97] developed a high temperature mechanism for n-butylbenzene. They compared computed results with experimental measurements of species concentrations from a low-pressure, lean, premixed, methane/n-butylbenzene flame and obtained satisfactory agreement. They further validated the n-butylbenzene mechanism by comparing computed results with measured species concentrations in a flow reactor at a temperature of 1060 K, pressure of 1 atm, and equivalence ratio of 0.98 [98]. Reasonable agreement was obtained.

2.5. Polyaromatics

Polyaromatics (also called polycyclic aromatic hydrocarbons) are fuel components with multiple aromatic rings with and without alkyl substitutions. The only polyaromatics for which chemical kinetic mechanisms have been recently developed that can be used as component models in a diesel surrogate are naphthalenes, which have two fused aromatic rings. Mati et al. [99] measured the species concentrations for 1-methylnaphthalene oxidation in a jet stirred reactor (JSR) at 800-1421 K, 1-10 atm and at $\phi = 0.5 - 1.5$. They developed a chemical kinetic mechanism for 1-methylnaphthalene and compared the computed results to their JSR measurements and the shock tube ignition measurements of Pfahl et al. [34]. Bounaceur et al. [100] developed a chemical kinetic mechanism for 1-methylnaphthalene and validated it by comparison to experiments in a shock tube (900-1500 K, 13 bar, stoichiometric) [101], flow reactor (1170 K, 1 atm, $\phi = 0.6, 1.0, 1.5$) [102], and jet stirred reactor (800-1100 K, 10 bar, stoichiometric mixtures). There is a need to obtain more experimental data on ignition delays for alkyl substituted naphthalenes in shock tubes and RCMs at conditions relevant to diesel engines (800-1200 K, 10–50 atm, $\phi = 0.5-3$). A lower limit temperature of 800 K is listed here because these compounds will probably not ignite on

a timescale relevant to diesel engines (milliseconds) below 860 K, based on the experimental data of Pfahl et al. [34].

2.6. Naphtho-aromatics

Naphtho-aromatics have molecular structures that contain saturated and unsaturated rings. Tetralin (also called 1,2,3,4-tetrahydronaphthalene) is a naphtho-aromatic and is similar to naphthalene except one ring is saturated. Yang and Boehman [72] investigated the oxidation of tetralin in a CFR octane-rating engine operated under motored engine conditions. They measured the products in the exhaust of the engine at an engine speed of 600 rev/ min, equivalence ratio of 0.25, intake temperature of 200 °C and a compression ratio range of 4.5-12.2. Unlike the previously discussed decalin, tetralin exhibited little low temperature chemistry in their motored engine. Tetralin mainly dehydrogenated to form 1,2-dihydronaphthalene and naphthalene. Ring opening reactions occur to a lesser extent for tetralin relative to decalin. No additional information could be found on the oxidation of tetrahydronaphthalenes in the peer-reviewed literature. However in his Ph.D. thesis, Wilk [103] studied the oxidation of mixtures of n-dodecane and tetralin in a constant volume vessel at 60-240 torr and 520-620 K. He added 5, 10 and 20% tetralin to n-dodecane. He found the addition of tetralin to n-dodecane increased the pressure where the onset of cool flames is observed for temperatures below 530 K. Above 530 K, the addition of tetralin has little effect on the pressure where the onset of cool flames is seen. He also found that the addition of tetralin increased the induction period before cool flames are observed. This effect was nonlinear with the 5% addition of tetralin having the largest effect and subsequent addition of tetralin having proportionally smaller effect. Indane is a naphthoaromatic with one aromatic ring and one unsaturated fivemembered ring. It has been studied in a jet stirred reactor at temperatures of 950-1350 K, equivalence ratios of 0.5 and 1, and a pressure of 1 atm by Dagaut et al. [104]. For indane oxidation at low fuel conversion, they measured intermediate products of indene, ethylene, toluene, benzaldehyde, benzene, styrene, and ethylbenzene, in order of decreasing concentration. At higher fuel conversion, they found large amounts of acetylene, methane, and phenyl acetylene. Pousse et al. [105] studied indane and methane mixtures in a low-pressure, laminar, flat flame burner at an equivalence ratio of 0.76. In addition to the products observed by Dagaut et al., they measured concentration profiles across the flame of xylenes, trimethylbenzenes, ethyl-toluenes, methyl-indane, naphthalene, phenol, benzaldehyde and benzofuran. In a subsequent paper, Pousse et al. [106] developed a chemical kinetic model for indane. They simulated their experiments for indane-methane mixtures in a low-pressure flame and the experiments of Dagaut et al. [104] for indane in a jet stirred reactor, obtaining satisfactory agreement.

2.7. Esters

Progress in the kinetic modeling of esters like those present in biodiesel was not covered in [1], but due to the increasing importance of biodiesel as a blendstock in diesel fuels worldwide, a brief review of advancements in this area seems justified and is provided here.

The first biodiesel-like ester to receive significant kinetic modeling attention was methyl butanoate (MB) [107]. The alkyl chain in MB consists of only four carbon atoms, which is shorter than the C16 and C18 chain lengths of the typical biodiesel esters shown in Fig. 2. Nevertheless, MB was viewed as a good starting point for biodiesel kinetic mechanism development because it is small enough to have a manageable number of species, yet large

enough that it could be expected to exhibit the negative temperature coefficient (NTC) autoignition-delay behavior characteristic of biodiesel esters with longer chain lengths.

The MB mechanism from Fisher et al. [107] was used with mechanisms for other oxygenated compounds by Curran et al. [108] to investigate oxygenate molecular structure effects on the formation of soot precursors under conditions similar to those found in a diesel engine. A later version of the detailed MB mechanism was used by Szybist et al. [109] in a zero-dimensional model of homogeneous charge compression ignition (HCCI) combustion and found to agree well with results from companion experiments in a single-cylinder HCCI engine.

Several studies have used reduced MB mechanisms based on the detailed mechanism in [107] to investigate biodiesel effects on engine combustion processes [110-112]. Brakora et al. [110] reduced the detailed MB mechanism from 264 species and 1219 reactions to 41 species and 150 reactions using flux analysis, ignition sensitivity analysis, and adjustment of reaction rate coefficients under constant volume conditions. The reduced MB mechanism was combined with a reduced n-heptane mechanism to successfully capture in multi-dimensional engine simulations the trends that were measured in engine experiments with biodiesel fueling and utilizing a conventional fuel-injection strategy [110]. Brakora and Reitz [111] went on to employ a modified version of the reduced mechanism in a single-zone simulation of HCCI engine operation to investigate the effects of biodiesel fueling on NOx emissions, and they found the effects to be small in general (<3% NOx increase with biodiesel). Ren et al. [112] used the reduced MB mechanism from [110] to conduct multi-dimensional engine simulations to investigate the effects of physical and chemical property differences between biodiesel and diesel on combustion processes and emissions. They found that chemical property differences (i.e., oxygen content and/or reactivity) play a large role in NOx emissions differences between the fuels.

Dooley et al. [113] reviewed previous work on mechanism development for MB and developed an updated mechanism for MB that was validated by comparing computed results to measurements in a variety of experimental apparatuses and over a wide range of conditions. Since the Dooley et al. [113] paper, there have been a number of studies on MB and similar esters. Gail et al. examined the effect of including mono-unsaturation in MB [114]. Huynh et al. [115] and Hayes and Burgess [116] used computational methods to identify important reaction pathways in MB and similar esters. Hakka et al. [117] used automatic mechanism generation to obtain chemical kinetic mechanisms for methyl and ethyl butanoates and validated the mechanisms using experimental data they obtained in a shock tube and a JSR. Toulson et al. [118] created an 8-step autoignition model for esters and alcohols based on the Shell Model [119] and used it to model ignition in an RCM.

Based on RCM experiments and simulations, Dooley et al. [113] asserted that MB actually does not exhibit the NTC behavior that was originally expected based on previous experiments and simulations in static reactors [107,120]. This observation has spurred investigation into the kinetics of esters with longer aliphatic chains that are more representative of the compounds present in biodiesel fuels produced from common feedstocks. A significant amount of attention has been focused on methyl decanoate (MD), a methyl ester with a C10 alkyl chain. A detailed kinetic mechanism for MD is reported by Herbinet et al. [121], and MD extinction and ignition have been studied experimentally in a non-premixed counterflow flame configuration by Seshadri et al. [122]. Hoffman and Abraham [123] conducted a computational study of HCCI combustion using a detailed kinetic mechanism for MD and, as was concluded in [111] for MB, found little if any increase in NO emissions when fueling with an ester vs. when fueling with an alkane

when the charge is fully premixed. Szybist et al. [124] experimentally studied MD combustion under HCCI conditions in a motored engine using Fourier transform infra-red (FTIR) spectrometry and gas chromatography/mass spectrometry (GC/MS). The FTIR results showed that MD produced significantly higher levels of CO2 during low temperature heat release relative to a gas-to-liquids diesel and a conventional diesel fuel, and the authors attributed this to decarboxylation of the ester group rather than oxidation. Analysis of the GC/MS results led to the conclusion that decarboxylation does not occur until the aliphatic chain of the ester has been largely consumed. Zhang et al. [125] conducted similar motored-engine experiments with the following C9 fatty acid esters: methyl nonanoate, methyl 2-nonenoate, methyl 3-nonenoate, and ethyl nonanoate. The highest reactivity was observed for the saturated ester ethyl nonanoate, followed by methyl nonanoate. The unsaturated esters had significantly lower reactivities, with reactivity decreasing as the location of the unsaturation moves toward the center of the aliphatic chain. They also found that decarboxylation does not occur during the early stages of oxidation. The effects of mono-unsaturation location on the oxidation of two related methyl esters with C10 alkenyl chains are reported by Herbinet et al. [126]. Consistent with the work of Zhang et al. [125], they found that methyl 5-decenoate is less reactive than methyl 9-decenoate because its unsaturation is closer to the center of the chain.

In addition to MD, a detailed kinetic mechanism has been reported for methyl octanoate by Togbe et al. [127], and species data from JSR experiments have been reported for methyl palmitate by Hakka et al. [26], a methyl ester with a C16 alkyl chain that is found in biodiesel made from typical biodiesel feedstocks (e.g., soy, rapeseed, palm). Glaude et al. [128] have added new classes of reactions and species to address the ester chemistry to the EXGAS software [48] which automatically generates reaction mechanisms. They tested the automatically generated mechanisms by successfully simulating experimental results of Dayma et al. for methyl hexanoate [129], methyl heptanoate [130] and their new experimental results for methyl decanoate in jet stirred reactors. Given the rate of progress in mechanism development for ever-morerepresentative biodiesel compounds, it is expected that full mechanisms for the methyl esters found in most common biodiesel fuels will be available soon.

3. Surrogate mixtures

Surrogate mixtures are mixtures of components used to represent the target, real fuel whose behavior one desires to model. The behavior of multi-component fuels is more complicated than single component fuels because species produced from one component can react with species from another component. These interactions often manifest themselves in the observed ignition delay times, flame speeds and other combustion characteristics of surrogate mixtures. The interactions need to be quantified by experiments and correctly simulated by chemical kinetic models so that combustion behavior of practical fuels can be accurately predicted. In the discussion below, recent research on surrogate mixtures is reviewed starting with binary mixtures and then progressing to more complex mixtures.

Honnet et al. [95] investigated the Aachen surrogate of 80% n-decane and 20% 1,2,4-trimethyl benzene used to represent JP-8 jet fuel. They performed experiments in a laminar, counterflow, diffusion-flame. They found that the Aachen surrogate had similar ignition and extinction characteristics, and measured soot concentrations compared to JP-8 in the counterflow flame. They developed a detailed chemical kinetic model to describe the Aachen surrogate and validated it over a wide range of conditions.

The predictions of the chemical kinetic model compared fairly well with their experimental measurements of ignition and extinction.

Lemaire et al. [131] have investigated the IDEA surrogate diesel fuel [132] which consists of 70% n-decane and 30% 1-methylnaphthalene (1-MN) and compared it to a low-sulfur diesel that contained 8% by volume esters. They investigated these fuels in an atmospheric pressure, flat flame burner with an injector tube in the center that nebulizes the liquid fuel and produces an aerosol. The flat flame burner is supplied with methane-air mixture. Based on laser induced incandescence (LII) of the soot and laser-induced fluorescence of the PAH (polycyclic aromatic hydrocarbons desorbed from the soot), they found that the IDEA fuel produced too much soot and PAHs compared to the low sulfur diesel fuel. Therefore, they reduced the amount of 1-MN in the surrogate fuel. To determine the amount of 1-MN, they used the threshold soot index (TSI) and matched the TSI of the surrogate and the diesel fuel. A surrogate with 20% 1-MN (instead of previously used 30%) matched the TSI of the diesel fuel. This new surrogate also matched the measured LII and PAH levels of the diesel fuel quite well (Fig. 6). Fig. 6 also shows that PAH is observed early in the flame when there is no soot and the opposite is seen late in the flame. This work supports the use of TSI to match the sooting behavior of the surrogate with the target real fuel [133-135], but it is not clear that fuel-induced changes in TSI quantitatively indicate the magnitude of fuel-induced changes in exhaust particulate matter (PM), soot, or smoke emissions from a diesel engine. When the researchers examined the PAHs absorbed on the soot, they found that the molecular weight distribution of the measured PAHs from the surrogate was narrower than the distribution from the diesel. Also note that the oxygenate content of the ester components in the low sulfur fuel likely reduced the levels of soot and PAH below those produced by a conventional diesel. This means that although the new surrogate works best compared to this diesel containing esters, the standard IDEA surrogate with 30% 1-MN may still work best in comparison to conventional diesel fuel. However, the findings of this work concerning how to match a surrogate fuel to a target real fuel are important.

Ramirez et al. [136] investigated the IDEA surrogate diesel fuel (70% n-decane/30% 1-methylnaphthalene, molar) in a jet stirred reactor at elevated pressures and compared it to a commercial low sulfur diesel fuel. The reactivity of the IDEA fuel, based on the measured CO profile, was similar to the commercial diesel from low to high temperatures and over a wide equivalence ratio range of 0.25–1.5 at 10 atm. A chemical kinetic model of n-decane and 1-methylnaphthalene showed reasonable agreement with their experimental data.

Kook and Pickett [137,138] investigated a surrogate of 23% m-xylene and 77% n-dodecane and compared it to a conventional jet fuel in a high pressure, high temperature, combustion-vessel used to simulate conditions in a diesel engine. Using planar LII, they showed that the surrogate fuel sooted more than the conventional jet fuel. They attributed this behavior to the surrogate fuel having a higher aromatic content than conventional jet fuel. Natelson et al. [139] tested the reactivity of a surrogate containing 50% n-decane/ 25% n-butylbenzene/25% n-butylcyclohexane in a pressurized flow reactor at 8 bar. This surrogate matches the maximum aromatic content allowed in jet fuel and the H/C ratio in a US average JP-8 jet fuel [3]. They also tested a surrogate containing 33% n-decane/33% n-butylbenzene/33% n-butylcyclohexane which was proposed to match diesel fuel properties. They used the amount of CO formation in the flow reactor as a measure of reactivity of the surrogate and the target fuels. They found these surrogates to be more reactive than the jet and diesel fuels they were designed to match.

In a series of studies from the same research group, Douce et al. [140] and Mathieu et al. [141] studied the sooting tendencies of



Fig. 6. Radial profiles of (a) laser-induced fluorescence of PAH and (b) laser-induced incandescence (LII) of soot particles obtained at different heights above the burner (HAB) in each flame. Surrogate 1 is original IDEA fuel of 30% 1-MN/70% n-decane. Surrogate 2 is new proposed surrogate of 20% 1-MN/80% n-decane. N-decane signals are very weak indicating near zero soot on this plot. The triangles and dashed line sometimes appear as solid lines. Reprinted from [131] with permission from Elsevier.

diesel surrogate components and a diesel surrogate mixture in a high temperature shock tube. In their first study, Douce et al. [140] examined the fuel components n-hexadecane, toluene, n-heptylbenzene, and 1-methylnaphthalene at temperatures of 1300 and 2700 K, pressures of 2–18 atm, under pyrolysis (without oxygen) and for two equivalence ratios (5 and 18). They measured the evolution of soot particles using laser light extinction. They measured soot induction time which is an indication of how rapidly a fuel will form soot. They found that 1-methylnaphthalene had the shortest soot induction times under pyrolytic conditions, followed by toluene and n-heptylbenzene. N-hexadecane had the longest soot induction time. They also measured soot yield which is the fraction of carbon in the fuel that forms soot. Under pyrolysis, 1-methylnaphthalene (C11H10) had the greatest soot yield (Fig. 7). At an equivalence ratio of 5 (which is probably more relevant to diesel combustion than pyrolysis) 1-methylnaphthalene had the largest soot yield, twice that of toluene.

In the second study from the same group and using the same experimental apparatus, Mathieu et al. [141] examined n-propylcyclohexane (PCH), n-butylbenzene (BBZ), 2,2,4,4,6,8,8-heptamethylnonane (7 MN) and a diesel fuel surrogate mixture of 39% PCH + 28% BBZ + 33% 7 MN by mass. Soot formation was investigated at temperatures of 1460–2570 K, pressures of 11–18 atm and under oxidative (equivalence ratios of 5 and 15) and pyrolytic conditions. Of the fuel components considered in the second study, they found that the soot induction times under pyrolytic conditions were shortest for n-butylbenzene, indicating it forms soot most rapidly. The next shortest induction time was the diesel surrogate mixture, followed by n-propylbenzene, and heptamethylnonane. Fig. 8 summarizes the results of both studies with 1-methylnaphthalene having the shortest soot induction times (not shown, but its induction times are slightly shorter than toluene) and n-propylcyclohexane having the longest time. It is somewhat surprising that a cycloalkane (n-propylcyclohexane) would have a longer soot induction time than an n-alkane (n-hexadecane),



Fig. 7. Soot yields from the pyrolysis of 1-methylnaphthalene ($C_{11}H_{10}$), toluene (C_7H_8), n-heptylbenzene ($C_{13}H_{20}$) and n-hexadecane ($C_{16}H_{34}$) at pressures of 10–18 atm and temperatures of 1350–2850 K in a shock tube. Reprinted from [140] with permission from Elsevier.



Fig. 8. Soot induction times for n-propylcyclohexane (PCH), n-butylbenzene (BBZ), 2,2,4,4,6,8,8-heptamethylnonane (7 MN) and a diesel fuel surrogate mixture (MIX) of 39% PCH + 28% BBZ + 33% 7 MN by mass [141]. Toluene (TOL), n-heptylbenzene (HBZ) and n-hexadecane (HDC) are from [140]. Reprinted from [141] with permission from Elsevier.

because literature studies indicate that cycloalkanes have higher particulate-matter formation tendencies (e.g. soot) than n-alkanes in diesel engines [142]. Mathieu et al. found further that n-butylbenzene produced larger soot yields under pyrolytic conditions than the other fuel components and diesel surrogate mixture considered. At an equivalence ratio of 5 (which was probably the equivalence ratio most relevant to diesel conditions), n-butylbenzene has the largest soot yield and n-propylcyclohexane is nearly as high. The diesel surrogate and heptamethylnonane yielded much less soot in comparison. It is interesting that, although n-propylcyclohexane is slow to start producing soot, it yields soot abundantly after its long induction period. This indicates that both the soot induction period and soot yield are important indicators of sooting tendencies of fuels.

Steil et al. [143] found that modeling predictions for a surrogate mixture of 70% n-decane/30% propylbenzene did not well represent experiments on shock tube ignition of kerosene.

Mati et al. [144] compared computed results of a five component mixture model with experimental measurements using a blended, synthetic diesel fuel in a jet stirred reactor (JSR) (T = 800 - 1400 K, $\phi = 0.5 - 2$, P = 1 and 10 atm). In the experiments, gas samples were extracted from the JSR with a fused silica probe and analyzed online and offline by gas chromatography with a flame ionization detector and mass spectrometry. Species profiles of some of the measured species are shown in Fig. 9. The amounts of the five components (23.5% n-hexadecane, 19% iso-octane, 26.9% n-propylcyclohexane, 22.9% n-propylbenzene and 7.7% 1-methylnaphthalene) used in the chemical kinetic model were chosen to match the amount of the various chemical classes in the synthetic diesel fuel (n-alkanes, isoalkanes, cycloalkanes, alkyl benzenes and two-ring aromatics). The reactivity of the synthetic diesel fuel, based on the CO and O2 profiles, was well reproduced by the surrogate model at 10 atm for the stoichiometric and fuel-rich case (Fig. 9), but not at 1 atm. The comparison of the predicted and measured intermediate species profiles in the JSR was similarly much better at 10 atm than at 1 atm. For the best comparisons (e.g., Fig. 9), the surrogate model was able to reasonably match many hydrocarbon intermediates and CO, but not CO₂. The chemical kinetic model did not include reactions to represent low temperature chemistry whose inclusion would likely improve predictions below 900 K. Because of poor agreement at 1 atm, further work needs to be done to investigate the effect of pressure in the experimental results and model simulations. The comparison of the experimental and modeling results seems to substantiate that CO is a good measure of agreement in fuel reactivity between the model and experiment. This is the same method of measuring fuel reactivity used by the Drexel group in their high pressure flow reactor [139]. When the comparison between the experimental and predicted CO was poor, the agreement of the rest of the species profiles was generally poor.

Myong et al. [145] experimentally investigated the injection of a diesel surrogate into a constant volume vessel filled with argon at a temperature of 400–700 K and a density of 5–20 kg/m³. A common rail fuel injector was used. They found that the high boiling point component of the diesel surrogate controls liquid phase length of the evaporating spray. In a later paper [146], they found that evaporation of the surrogate fuel is promoted by addition of a low boiling point component because the saturated-vapor pressure line of the high boiling point component shifts to a lower temperature in the two-phase region.

In future work on surrogate fuels for diesel, surrogates need to be investigated that contain components that are more representative of the carbon range in diesel fuel (C10–C22) [1]. There is a lack of representative components on the high end of the carbon range. Also, iso-alkanes need to be added to the surrogate in the appropriate carbon range.

With respect to biodiesel esters, combined mechanisms for representative esters with C16 and longer aliphatic chains have not been reported. Nevertheless, some experimental measurements are available to assist in the development of biodiesel surrogates. In addition to the physical property data for esters presented in the "Physical Properties" section of this paper below, some reactivity data have been published. Dagaut et al. [147] studied the oxidation kinetics of rapeseed methyl ester (RME) in a JSR. They found that simulations using detailed n-hexadecane kinetics yielded reactivity characteristics closely matched to those measured for RME. Bamgboye and Hansen [148] used composition and ignition quality data reported for various biodiesel blends from the literature in a regression analysis to develop an equation relating the cetane number of a mixture of methyl esters to the weight percentages of its constituent compounds.

4. Reduction of detailed chemical kinetic mechanisms

There are many ways to reduce the computational costs of including fuel chemistry in reacting flow models. The most obvious way is to reduce the number of species and reactions in the mechanism, while maintaining the accuracy required for a given application [149,150]. This reduction can be done by creating skeletal mechanisms and by lumping of species [151]. Skeletal mechanisms can be formed by a variety of methods including directed-relational graph [152] and reaction flow analysis [153]. Further computational gains can be made by accounting for species that are in steady-state [154] or partial equilibrium. An alternative to reducing the size of the detailed mechanism is to save computational time by precalculating the chemistry and using table lookups [155]. Mechanism reduction can be done "on the fly" during a reacting flow calculation, so that much smaller mechanisms can be used at different times and locations on the computational grid [156,157]. There are other ways to reduce computational times. The computational efficiency of chemistry solvers can be improved [158]. The chemistry can be solved on a coarser computational grid than the flow dynamics, as is done in multizone homogeneous charge compression ignition (HCCI) engine calculations, which resulted in large computational



Fig. 9. Comparison of a surrogate diesel model and synthetic diesel fuel experiments in a jet stirred reactor at 10 atm and $\phi = 2$ (diesel, 0.05%; O₂, 0.345%; N₂, 99.6%; residence time = 0.5 s). The modeling predictions are curves with small symbols and the experimental data are large symbols. Reprinted from [144] with permission from Elsevier.

speedups [159]. These methods and others have been reviewed recently by Lu and Law [160].

There has been much recent work on how to reduce chemical kinetic mechanisms and their associated computational costs. Lu and Law and co-workers have a series of papers on the directed-relational graph (DRG) method for mechanism reduction and stiffness removal for further computational cost reduction [122,160,161]. After performing DRG, lumping, quasi steady-state analysis (QSSA) and stiffness removal, they reduced a 561-species and 2539-reaction n-heptane mechanism [17] to 52 species and 48 global reactions, while maintaining accuracy on target calculations for extinction in a perfectly-stirred reactor and constantpressure ignition over a wide range of temperature and pressure [160] (Fig. 10). Prager et al. [162] also reduced Curran et al's nheptane mechanism, but used the method of computational singular perturbation (CSP) [163]. They got good agreement for nheptane premixed flames over a range of equivalence ratios and pressures. They were able to reduce the n-heptane mechanism to 66 species and 326 reactions. Neimeyer et al. [150] combined the DRG method with sensitivity analysis and error-propagation to reduce an n-decane mechanism of 940 species and 3887 reactions to a skeletal mechanism containing of 211 species and 794 reactions. Pepiot-Desjardins and Pitsch [164] also used the DRG method and developed an approach to reduce a mechanism based on prediction of a series of targets, like ignition delay time, with a user-defined error tolerance. Sun et al. [149] have developed a direct path flux analysis method for generating skeletal mechanisms and found greater accuracy for a similar reduction in number of species than the DRG method over a wide range of pressures and temperatures.

Hughes et al. [154] reduced an n-heptane mechanism of 358 species and 2411 reactions created by EXGAS [48] to a skeletal mechanism. Using QSSA, they further reduced the mechanism to 81 species and 341 reactions while retaining accurate reproduction of low and high temperature chemistry of the detailed reaction mechanism.

Nagy and Turányi [165] have developed an approach where strongly connected sets of species in a detailed mechanism are identified and added to a test mechanism in sequential steps, while checking for errors by comparison with simulations using the fully detailed model. Multiple test mechanisms were developed. The test mechanism with the smallest error and least CPU requirement was selected. They reduced a surrogate fuel mechanism with 345 species and 6874 reactions to 47 species and 246 reactions and obtained a computational speedup of 116 times in a zero-dimensional, methane-air, homogeneous reaction problem.

Chen and Tham [166] developed a more efficient method to solve for quasi steady-state (QSS) species in reduced chemical kinetic mechanisms. They identify QSS species that are strongly coupled and solved for them separately using a fixed point iteration and matrix inversion method. They saw speedups of a factor of 20 for a primary reference fuel mechanism (n-heptane and iso-octane) with 101 regular species and 251 quasi steady-state species.

Janbozorgi et al. [167] used the rate-controlled constrainedequilibrium (RCCE) method to obtain faster chemistry solutions and tested it for the case of methane oxidation. The RCCE method was first developed in 1971 by Keck and Gillespie [168]. It is based on the principle that slow reactions impose constraints on the chemical system and control the rate at which the system relaxes to chemical equilibrium, while fast reactions equilibrate the system to the constraints imposed by slow reactions [167]. By using 12 constraints, they were able to reduce the number of reactions from 133 to 20 in RCCE calculations. Rigopoulos et al. [169] combined the RCCE method with the level of importance (LOI) method which is related to the CSP method and uses timescale analysis to determine which species must be retained in the mechanism. They obtained a combined speedup of over a factor of 10 for a propane mechanism with 117 species and 665 reactions in a laminar flame calculation. König and Mauss [170] have developed an on-demand, intrinsic low dimensional manifold (ILDM) method to reduce the computational requirements of detailed chemical kinetic mechanisms when calculating chemically reacting flows. Normally, the ILDM method requires the calculations of an ILDM table that covers the whole state space that is expected to be accessed by the computation. In the on-demand scheme, only the part of the ILDM table that is needed is generated "on the fly" during a reacting flow simulation. For a laminar flame calculation for syngas (H₂/CO), they saw an 82% savings in computer memory storage using the on-demand scheme compared to the usual method of pre-calculating the ILDM table ahead of time. Pera et al. [171] have also used an ILDM method and implemented it in a multi-dimensional CFD engine code. They use a reaction progress variable with a tabulated



Fig. 10. Flow chart of the integrated reduction procedure for an n-heptane mechanism. Reprinted from [160] with permission from Elsevier.

chemical source term to further reduce computational requirements associated with chemistry. They have demonstrated their approach with two simulations of a single-cylinder diesel—engine cycle using n-heptane as a surrogate fuel for diesel.

Singer and Green [172] developed an adaptive orthogonal decomposition method to solve the reaction—diffusion equation in reacting flow problems. The minor species mass fractions are projected on to a reduced dimensional space so that the number of equations governing the chemistry is reduced. For a one-dimensional, methane-air, premixed, laminar flame, they saw a speedup of 3.5 times in the reacting flow computation using GRI Mech 3.0 [173].

Gu et al. [174] have developed a dynamic multi-timescale (MTS) method to significantly decrease the computational costs of including chemistry in reacting flow problems. They combined the MTS method with an implicit Euler scheme to further increase computational efficiency. Their approach was tested by computing hydrogen, methane and n-decane ignition delay times and a spherical flame with speedups of up an order of magnitude.

Oluwole et al. [175] have developed a method that determines the range of validity (pressure, temperature and equivalence ratio) for a given reduced mechanism.

Another way to reduce computational costs associated with chemical kinetic models in CFD calculations is to reduce the number of zones for which chemistry has to be solved in the computational domain. This is an attractive method because it reduces the total computational resources required for solution of the chemistry without the user having to devote effort in reducing the size of the chemical kinetic mechanism. Aceves et al. [176] first proposed such a method to reduce computational costs in HCCI engine calculations. In a subsequent paper, Babajimopoulos et al. [177] further refined the method with an automated mapping of computational zones with similar temperatures and equivalence ratios on to a reduced set of zones for which chemistry is solved. After the chemistry calculation, the updated species concentrations and internal energies are mapped back on to the fully-resolved computational grid. They tested the approach by performing a premixed charge compression ignition (PCCI) engine calculation using KIVA-3 V [178], methane as the fuel and GRI Mech 3.0 [173] (53 species and 325 reactions). They found that the computational time was reduced by more than 90% by using the new multizone approach compared to solving the chemistry in every computational zone or cell. The approach was later tested on a larger mechanism (iso-octane [45] with 857 species and

3605 reaction) for an HCCI engine simulations using KIVA3 V-MZ-MPI [179]. Computed results were compared with detailed experimental measurements of species in the engine exhaust for fuel/air equivalence ratios of 0.08–0.28. Excellent agreement was obtained between predicted and measured concentrations of many engineout species such as unburned fuel, formaldehyde, and many other intermediate hydrocarbon species. Recently, Goldin et al. [180] developed a cell agglomeration (CA) technique that combines computational zones that have similar species compositions and reduces the number of zones for the chemistry solver. They saw speedups of 2–11 compared to runs without the CA method in a 2-D premixed flame and an axisymmetric, partially-premixed, engine simulation with methane as the fuel. The error tolerances chosen for these runs varied from 1 to 10%.

An additional way to reduce the number of zones in which the chemistry has to be solved is adaptive mesh refinement (AMR) [181–183]. This method reduces the total number of zones or mesh cells in the entire computational grid by placing more zones in regions of high activity. The domain is first coarsely gridded with mesh cells. As a region of the mesh develops more activity and gradients, these coarse mesh cells are refined by dividing each mesh cell into smaller cells. As the gradients are reduced and a region becomes more homogeneous, the refinement of the mesh can be removed. Therefore, the total number of mesh cells in which the chemistry has to be solved is reduced because of the use of a course grid where refinement is only added as needed and removed when no longer needed. The criteria used to specify where more zones are added or removed are defined by the user or the computational code. For example, Day et al. [184] used criteria of high concentration of hydrogen peroxide (H₂O₂) and high magnitudes of the fluid vorticity to specify the location of mesh refinement in a two-dimensional, hydrogen flame. Most of the effort in AMR has been on one- or two-dimensional meshes, although some work has been done on 3-D meshes [185,186]. Additional work needs to be done to develop reliable algorithms for 3-D meshes needed for CFD calculations in internal combustion engines. When reliable and tested algorithms become available, this will be a very attractive approach because it can be automated, without much user involvement.

Liang et al. [157] used a dynamic adaptive chemistry strategy to reduce the chemistry "on the fly" in a reacting flow calculation. For a zero-dimensional, single-zone, HCCI engine calculation, they obtained a 70-fold CPU time reduction with a 1099 species mechanism of a gasoline surrogate fuel. He et al. [187] also used an "on the fly" reduction approach that consisted of chemical flux analysis and dynamic generation of reduced mechanisms. They saw a speedup of a factor of 40 for a detailed chemical kinetic mechanism for n-pentane [17] with 385 species and 1895 reactions when simulating a computationally intensive calculation of a pairwise mixing stirred reactor.

It is difficult to determine the best methods to reduce detailed chemical kinetic mechanisms and their associated computational costs. Combined techniques, as promoted by Lu and Law [160], are likely to be a successful approach and used in future work. It is also likely that improvements in the numerical solvers [158,172] will be combined with mechanism reduction techniques. Techniques such as CSP and principle component analysis may be more useful as tools to interrogate reaction mechanisms and to determine the controlling rate processes [188], than as mechanism reduction tools. Lu et al. [189] used chemical explosive mode analysis (CEMA) that defined an explosive index (EI) for each species based on the concept of a radical pointer in CSP. El is the normalized contribution of a species to a chemical explosive mode, which is associated with a positive eigenvalue in the chemical Jacobian. The magnitude of the explosive index can be used in an ignition calculation to identify important species that lead to ignition. Another way to reduce computational costs is speeding up the chemistry solvers because it does not require the user to devote the time and effort to reduce the size of the mechanism. A faster chemistry solver called a sparse matrix solver was recently included in Chemkin [190]. In the long term, "on the fly reduction" likely will be employed because the reduced mechanisms produced need not be valid over the whole solution domain with this method, leading to greater mechanism reduction and computational speedups. Also "on the fly" methods do not require user time in performing lengthy mechanism reduction calculations.

5. Selection of surrogate mixtures to represent diesel fuel

Once a palette of surrogate compounds is available, a procedure is needed to select the surrogate compounds and their amounts that will be included in a surrogate fuel. Various procedures have been examined and discussed in the literature [4,5,133,191].

Zhang et al. [191] matched chemical composition of a surrogate fuel to the target practical fuel (JP-8, a common aviation fuel) by using nuclear magnetic resonance (NMR) analysis. They tried to match as closely as possible the relative amounts of each type of carbon atom identified by NMR in the surrogate and the target fuels. The types of carbon atoms identified included those bonded to primary, secondary and tertiary H atoms. Other types of carbon atoms considered were aromatic carbons bonded to an H atom or to a carbon substitute. Carbons attached to bridges across cyclic compounds were identified, as well as additional types of carbon atoms. Finally, an attempt was made to match the relative amounts of eight types of NMR-classified carbon atoms in the surrogate and the target fuel.

Colket et al. [133] discussed the combustion and physical properties that are important to match between a surrogate fuel and a target practical fuel. In the case of jet fuel, they stated that H/C ratio, amount of each chemical class (e.g. aromatics), heat of combustion, smoke point [134], viscosity and distillation curve were the most important properties to match. Instead of smoke point, threshold sooting index (TSI) [135] and yield sooting index [192] could alternatively be used for accessing the sooting propensity of the fuel. To match chemical composition, they suggested NMR analysis [191]. They outlined an approach for how the above surrogate properties can be estimated based on the composition of a proposed surrogate.

Dryer et al. [5] presented a method for specifying a surrogate fuel composition for jet fuel. They advocated matching the following properties in the surrogate and the target jet fuel: C/H ratio, threshold sooting index (TSI), and cetane number. They stated that it is important to match the C/H ratio because it affects surrogate properties such as flame temperature, heat of reaction, flame speed, and the local locations where fuel/air stoichiometry is one for non-premixed systems. In addition, C/H ratio of the surrogate fuel affects the total air/fuel flow rates through a combustion device. They recommend using cetane number to match the ignition properties of the surrogate and jet fuel. Because of its ease of use, repeatability and accuracy, they also recommend using the IQT test [193] to determine derived cetane numbers for surrogate components, their mixtures and the target fuel.

Puduppakkam et al. [4] presented an approach where the component type and quantity in a surrogate fuel were determined by matching a number of properties of the target fuel. The proposed properties to be matched in the target fuel were lower heating value, C/H ratio, distillation curve, and ignition quality. Since the target fuel in this case was gasoline, octane number was used as a measure of ignition quality. For diesel, cetane number can be used. The distillation curve is matched by matching the T10, T50

and T90 points, where T10 is the mixture boiling temperature where 10% of the liquid fuel volume is distilled. An iterative approach was used to determine the composition of the surrogate (as shown in Fig. 11).

In future work on surrogate fuels, many of the above characteristic properties will likely be used to specify surrogates for practical fuels, including NMR to specify chemical composition, C/H ratio to ensure proper flame temperatures, cetane number for ignition quality, threshold sooting index for sooting propensity, and a method for specifying a proper distillation curve. However, these properties are global indicators for an initial selection of a surrogate fuel. Further refinement of the surrogate selection can be made by comparing the surrogate and target fuel behavior in fundamental laboratory devices like shock tubes, flow reactors, jet stirred reactors, rapid compression machines, and premixed and non-premixed flames. For diesel spray properties, constant volume combustion chambers can be used to assess the spray characteristics of the surrogate and target fuel [146,194]. Finally, engines that provide optical access to the combustion chamber and allow the application of laser/imaging diagnostics can provide validation data for surrogate fuels in practical combustion devices.

6. Physical properties

Physical properties for surrogate components, their mixtures, and target real fuels are needed to simulate combustion of diesel fuel in internal combustion engines. When experiments are performed, the physical properties of the diesel surrogate fuel need to match those of the target fuel so that their injection, vaporization, and mixing characteristics are similar. In a recent paper on a computational fluid dynamic model for diesel combustion [195], the physical properties of the liquid needed to simulate the diesel spray were density, vapor pressure, surface tension, viscosity, thermal conductivity, heat of vaporization, and heat capacity. The properties of the gas phase species needed were species diffusivity, thermal conductivity, viscosity and heat capacity. This work showed that it is important to properly treat the vaporization properties of a surrogate diesel fuel. In their simulations using a sixcomponent surrogate for diesel fuel, Ra and Reitz demonstrate that



Fig. 11. Flow chart for developing model fuels for gasoline [4]. Reprinted with permission from SAE paper 2009-01-0669 © 2009 SAE International.

light components are more prevalent in the upstream gases of a diesel spray, while heavy components are more prevalent downstream (Fig. 12). Other physical properties that are needed to develop surrogate fuel models are transport properties of the species in the gas phase (viscosity, thermal conductivity, species transport). As discussed below, Holley et al. [196] show that the most important species for which accurate gas phase species transport are needed are the fuel components and the light species (OH, H, O, O₂, CO₂ and H₂O), particularly O₂. Recent progress in improving the knowledge of physical properties of surrogate components, their mixtures and real fuels is discussed below.

Holley et al. [196] proposed transport properties for n-alkanes up to tetradecane and 1-alkenes up to dodecene based on correlations of corresponding states [197]. They used these new transport properties to model the propagation and extinction of n-dodecane flames. They were able to quantify the relative importance of chemical kinetics and transport properties on flame propagation and extinction. In this paper and a subsequent paper [198], they identified the critical species for which accurate species transport are needed to accurately calculate flame speeds and extinction. Calculations of laminar flame speed showed a high sensitivity to the diffusion coefficient for O₂ and some sensitivity for H, O and OH. Calculations of flame extinction showed a high sensitivity to the diffusion coefficients of the fuel, OH, H, O, O₂, CO₂ and H₂O.

For liquid fuel properties, Caudwell et al. [199] measured the viscosity and density of five hydrocarbons (octane, decane, 1,3-dimethylbenzene, 1,2,3,4-tetrahydronaphthalene, and 1-methylnaphthalene) over a temperature range of 298–473 K and a pressure range of 0.1–200 MPa. The measurements had relative uncertainties of 2% for viscosity and 0.2% for density. Correlations for density and viscosity were developed and compared to literature data.

Hernández-Galván et al. [200] experimentally measured the liquid viscosity of cyclohexane and mixtures of cyclohexane with tetradecane and benzene over a temperature range of 331–393 K and a pressure range of 0.7–60 MPa. They developed viscosity models that were able to satisfactorily represent the viscosity of the binary systems over the entire pressure, temperature and composition range studied.

Perkins et al. [201] measured the thermal conductivity of methylcyclohexane and propylcyclohexane over a wide range of temperature (300-600 K) and pressure (0.1–60 MPa). They used the experimental data to develop correlations for thermal conductivity that are estimated to have a relative uncertainty of 4% at a 95% confidence level.

Bruno et al. [202,203] have developed an approach called the advanced distillation curve (ADC) for measuring distillation curves for practical fuels that measures the true thermodynamic state of the fluid. The technique obtains accurate temperatures, pressures and volumes so that the results can be used for equation of state development for the fuel. Equations of state provide functional relationships of density, pressure, temperature and provide other thermodynamic quantities such as heat capacity. Bruno et al. also use gas chromatography and mass spectrometry to characterize the various distillation fractions of the fuel. Work from this group includes data for petroleum-derived fuels as well as neat biodiesel and mixtures of biodiesel with petroleum diesel [202,204,205]. Such characterizations are needed to specify the vapor composition in the vicinity of fuel droplets in diesel combustion simulations and to validate multi-component vaporization models.

Huber et al. [206] developed a surrogate mixture model to represent the physical properties of a coal-derived liquid fuel. They used gas chromatography with mass spectrometry to analyze the composition of the coal-derived fuel. The coal-derived liquid was mainly composed of cyclic alkanes, especially decalins. An ADC



Fig. 12. Computed concentration of vaporized hydrocarbons in a surrogate diesel spray from a multi-component vaporization model at 0.5 ms after start of injection. The gray filled circles represent droplets in the spray. The color-filled contours and legend give the vaporized fuel mass fractions. The interval of iso-contours is 0.025. MW is the average molecular weight of the vaporized hydrocarbons at the given location in the spray. The left bar chart shows the vaporized component concentrations upstream near the injector tip, while the right bar chart shows concentrations downstream at the tip of the spray plume. Reprinted from [195] with permission from Elsevier.

method was used to obtain the distillation properties of the coalderived fuel. From the experimental data obtained, they developed a five component surrogate model (n-propylcyclohexane, transdecalin, alpha-methyldecalin, bicyclohexane, and n-hexadecane) that was able to predict density, speed of sound and viscosity of the target coal-derived fuel within 1, 4, and 5%, respectively, of available experimental data. A low and high molecular weight compound was included in the surrogate to properly predict the initial boiling point and the tail of the target distallation curve. Later, they applied the same approach and derived a seven component surrogate fuel for a Fischer-Tropsch S-8 jet fuel [50]. The seven components were n-nonane, 2,6-dimethyloctane, 3-methyldecane, n-tridecane, n-tetradecane, n-pentadecane and n-hexadecane. These components were selected from a list of components actually measured in the S-8 jet fuel. The amount of each component was optimizied to obtain the best agreement with the experimentally measured density, viscosity, sound speed and distillation curve of S-8 jet fuel. They found that the overall shape of the distillation curve of the surrogate is determined by only four components. However, small amounts of a low and a high molecular weight n-alkane were added to the surrogate to achieve the desired initial boiling behavior and the proper tail of the end of the distallation curve. The inclusion of branched hydrocarbons was necessary to accurately simulate the thermal conductivity of the target fuel. The approach that Huber et al. have developed also can be applied to matching diesel surrogate fuels to real diesel fuels.

For biodiesel esters, thermochemical property data estimated using various computational techniques recently have been reported by Osmont et al. [207] and Lapuerta et al. [208]. Ott et al. [209] measured densities and sonic speeds of the five primary fatty acid methyl esters found in biodiesel fuels produced from soybeans and/or rapeseed. These data can be used to develop equations of state for the individual methyl esters. Once equations of state for the individual methyl esters are known, a model can be developed to estimate the thermodynamic properties of mixtures of the esters. This was done by Huber et al. in [210] for soy-derived biodiesel, wherein predictions for density, speed of sound, and bubble point were found to agree well with values measured from two soy biodiesel samples. Yuan and co-workers have conducted a number of studies of the physical properties of biodiesel fuels and their constituent methyl esters. In [211], they presented and applied methods for determining biodiesel physical properties including critical properties, vapor pressure, latent heat of vaporization, density, surface tension, and liquid viscosity, and achieved good agreement with the limited available published data. In [212], they predicted the temperature-dependent vapor pressures and normal boiling points of 14 fatty acid methyl esters and 19 biodiesel fuels with good agreement to reported data. They observed that uncertainty in the normal boiling point of methyl linoleate is a primary factor affecting the predicted normal boiling points of the biodiesel fuels. In [213], they reported measurements of the kinematic viscosities of four biodiesel fuels and their 25, 50, and 75% blends with #2 diesel over a range of temperatures from 20 to 100 °C. Relationships between viscosity and temperature for the biodiesel fuels were found to be similar to those for diesel fuel. The work also provides a relationship that can predict the viscosity of a biodiesel fuel if its specific gravity is known. The work on biodiesel viscosity was extended in [214], which provides a method to estimate viscosity if the fatty acid methyl ester composition is known. Agreement with experimental data was again good, with maximum errors of 7% or less. Finally, a wide range of detailed property data (including critical properties, vapor pressure, liquid density, liquid surface tension, and latent heat of vaporization, as well as liquid and vapor heat capacities, viscosities, and thermal conductivities) for several biodiesel compounds are available by subscription to the Design Institute for Physical Properties (DIPPR) database [215].

7. Recommendations

A general theme from the above review is that data are required for compounds with higher molecular weights as well as molecular structures that are more representative of compounds found in market diesel fuels. Having accurate compositional data for market diesel fuels is therefore an important step in creating representative diesel surrogate fuels, and work to quantify typical compositions and variabilities among market diesel fuels would be of value. The recent technical report by Alnajjar et al. [216] is an excellent exposition of the types of analytical techniques that can be employed to characterize diesel fuels and thereby assist in the development of improved diesel surrogates. Also, it would be helpful to better understand the compositional characteristics of current and expected future blending streams (*e.g.*, those obtained through Fischer—Tropsch processes; upgrading of oil sands, oil shale, and coal deposits; pyrolysis; hydrotreatment of bio-derived oils; biological processing of biomass; *etc.*).

Relevant target fuel compositional information can be used to guide the selection of individual pure compounds for use in formulating the surrogate. A set of pure compounds used to formulate a surrogate is termed a surrogate palette. Successful diesel surrogate palettes, while clearly dependent on target fuel properties and application requirements, are likely to include n-, iso-, and cyclo-alkanes, as well as aromatics and tetralins, in approximately the C8-C22 range. The iso-alkanes are likely to have one (or perhaps two) methyl branches near one end of the chain. The cyclo-alkanes and aromatics are likely to have one ring with multiple shorter-chain substitutions. Unfortunately, aside from the n-alkanes, representative diesel fuel components are typically difficult and expensive (5000/kg) to procure at high purity ($\geq 98\%$), and as a result, the literature contains only limited (if any) thermophysical and chemical characterization data for them. Hence, it is recommended that high purity sources of these compounds be developed (e.g., by custom synthesis or through separation and purification from actual refinery streams). A centrally administered effort could take advantage of economies of scale and accelerate progress by providing these compounds to the research community at a lower cost. In addition, if sufficient quantities of the pure compounds could be obtained, a time-invariant diesel surrogate fuel could be developed and provided to the community as a highprecision standard reference material.

The generally limited availability and higher cost of representative diesel range pure hydrocarbon compounds makes it advisable to select the surrogate palette carefully. If the chemical complexity of the surrogate is greater than necessary, then fuel costs and computational costs to use the surrogate will be unnecessarily high. To avoid this outcome, engine and/or combustionvessel data acquired using well-characterized target fuels should be compared to data obtained at the same conditions using corresponding surrogate fuels. These results should show how accurately compositional, volatility, ignition quality, and/or other characteristics must be matched in order for the surrogate to reproduce the desired behaviors of the target fuel. Of course the degree of chemical fidelity required is likely to depend on what combustion parameters need to be matched, the accuracy required for this matching, and what combustion strategy is being used.

The best approach for detailed kinetic modeling of biodiesel fuels may be more straightforward than for petroleum-derived fuels because biodiesel fuels typically are composed of such a small number of distinct ester compounds (<10) [12]. In this case, it could be advisable simply to develop kinetic models for each of the pure compounds in the biodiesel and combine them to produce a mechanism that is perfectly representative of the target biodiesel. In this case, no surrogate mechanism is required, since the oxidation of all of the compounds in the target fuel can be computed directly.

Once they have been identified, methodologies for formulating successful diesel surrogates should be reported in detail. Easy-touse software tools also would be of great value for assisting in the formulation of optimal diesel surrogates, given desired matching criteria between the target and surrogate fuels.

Fundamental physical and transport property data will be needed for each of the pure compounds comprising any surrogate palette. Chemical characterization data should be acquired in fundamental experiments such as shock tubes, jet stirred and variable-pressure flow reactors, and rapid compression machines to determine not just ignition delay times, but also species histories. Species histories are essential for the rigorous validation of each chemical kinetic mechanism for each pure compound in the palette. Nevertheless, a lack of species-history data should not hold up the development of detailed kinetic mechanisms for each of the compounds in the palette. Rather, mechanisms should be developed and refined in parallel with the acquisition of the corresponding species-history data. In addition, it would be of interest to compare pure compound ignition delays measured using an IQT to those measured using more fundamental experiments and elucidate the reasons for any observed discrepancies, since the IQT is becoming such a standard platform for characterizing fuel reactivity.

Submodels for the individual pure compounds in a palette must be combined to develop accurate models for the behaviors of their mixtures. Specifically, validated mixture models should be developed for chemical kinetics (including ignition delay and species), volatility, and transport properties. These models, especially those for chemical-kinetic processes, should be reduced to be as simple as possible while still achieving the required accuracy. This is essential if the surrogate is to be employed in practical CFD-based optimizations of engine designs, which is ostensibly the ultimate goal of surrogate development efforts. The kinetic mechanism reduction process should be automated and include error estimation. Faster chemistry solvers would be of significant value for enabling computationally tractable surrogate models.

Finally, carefully controlled measurements should be made with the surrogate fuel in engine or combustion-vessel experiments, and the results should be compared with CFD results at the same conditions. These comparisons should be made for various combustion strategies and over a wide range of operating conditions within each strategy. This will assist in determining the extent to which combustion models using the surrogate actually reproduce the physical and chemical processes of interest in practical combustion devices. The surrogate palette, formulation methodology, kinetic models, property data, *etc.* can then be refined and/or supplemented until predictive modeling capability is achieved.

8. Summary

Recent advances in the development of surrogate fuels for diesel have been reviewed. For the chemical class of large n-alkanes, there has been considerable progress made on chemical kinetic modeling and experimental investigations. Significant progress also has been made in all the fuel classes of iso-alkanes, cycloalkanes and aromatics. However, limited work on the fuel class of tetrahydronaphthalenes (tetralins) could be found in the literature. For reducing the large chemical kinetic models that result from surrogate fuel model development, significant progress has been made on new mechanism reduction methods.

Recommendations for future work have been made. With regard to pure components, fundamental experimental data is needed to fill out the higher carbon range of diesel fuel (C15–C20). This is difficult to do experimentally because of the high boiling point of these hydrocarbons and computationally because of the large number of species and reactions that are needed. There is a considerable gap in the work on the iso-alkane chemical class. The iso-alkanes in diesel fuel are lightly branched with one or two methyl side groups. No fuel component models or experimental measurements of such hydrocarbons in the carbon range of diesel fuel have been made to the author's knowledge. For cycloalkanes

and esters, most of the work has been done on the light end of the carbon range of diesel fuel and biodiesel, respectively. For work on multi-component surrogate fuels, there is again a lack of work on surrogate fuels that have components to represent the high molecular weight end of diesel and biodiesel fuels.

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