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Thèse de Doctorat

Radwan ALKHATIB

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Development of an alternative fuel from waste of used tires by pyrolysis

JURY

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Abstract and keywords

The objective of this work is to get alternative fuel comparable with the available diesel in the market following the EN590. The fuel getting was via optimization of pyrolysis conditions which are temperature, heating rate (power of electrical resistance) and inert gas flow rate. The optimum values are 465°C, 650 Watts and without inert gas flow rate. Inert gas role is limited to purge the system for 30 minutes before start the pyrolysis to get rid of oxidative gases. The obtained product is comparable with the diesel as it has GCV 45 KJ/kg, low density of 0.85 and 7% tar content.

Keywords: pyrolysis, waste tires, fuel, motor.

Résumé et mots-clés en français

L'objectif de ce travail est de valoriser des déchets de pneus usagés par pyrolyse afin d'obtenir un nouveau carburant comparable avec le gazole suivant la norme EN590. L'obtention de ce carburant était réalisée via l'optimisation des conditions de pyrolyse qui sont la température, la vitesse de chauffage (puissance de la résistance électrique) et du débit d'azote. Les valeurs optimales sont 465°C, 650 Watts et sans azote. Le rôle de l'azote est limité à purger le réacteur avant le début de la pyrolyse pendant 30 minutes pour évacuer l'air hors du système. Le carburant produit est comparable au gazole avec un pouvoir calorifique supérieur de 45 MJ/kg, une densité de 0.85 et une teneur en goudron 7%.

Mots clés : Pyrolyse, pneus usagés, carburant, moteur.

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Chapter 1
Introduction and Bibliographic study

1-I Introduction

The energy crisis and environmental degradation are the main problems mankind is facing today. These problems owe their origin to a growing population, rapid industrialization and huge quantities of solid refuse, which are generated daily. To alleviate part of our energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for the possible recovery of resources from non-conventional sources, like municipal and/or industrial wastes, refused plastics, scrap tires…etc. The disposal of these organic solid wastes from human activity is a growing environmental problem for modern society, especially in developing countries. The scrap tire is one of the very common and most important hazardous solid wastes all over the world [1].

The disposal of scrap tires is a major environmental problem, because scrap tires in open areas demand valuable landfill space and may result in accidental fires with pollution emissions, such fires are difficult to contain because of the tires' high flammability and because of the pockets of air present in the piles. One fire in Huntington, VA, burned for nine months [2]. They can also serve as a breeding ground for mosquitoes and vermin, as well as, scrap tires present an eyesore. The nuisance caused by the scrap tires is majorly because they immune to biological degradation and can last for several decades if no proper handling is carried out. As a result, significant attention has been paid to scrap tires disposal.

With the continued world-wide increase in production of automotive cars and trucks, the generation rate of scrap tires is increasing dramatically. For example, the world generation of scrap tires in 2005 was over 2.5 MT in North America, 2.5 MT in Europe and 0.5-1MT in Japan. To become, nearly 3.4, 4.6 and more than 1million tons of scrap tires were generated within USA, Europe and Japan in respect in 2007[3, 4, 5]. According to these estimations, this figure will increase to above 17 MT per year by 2012; figure 1-1. In china as well, it was 3.2MT in 2004 [6]. Others estimate that 1 billion post-consumer tires are arising per year [7].

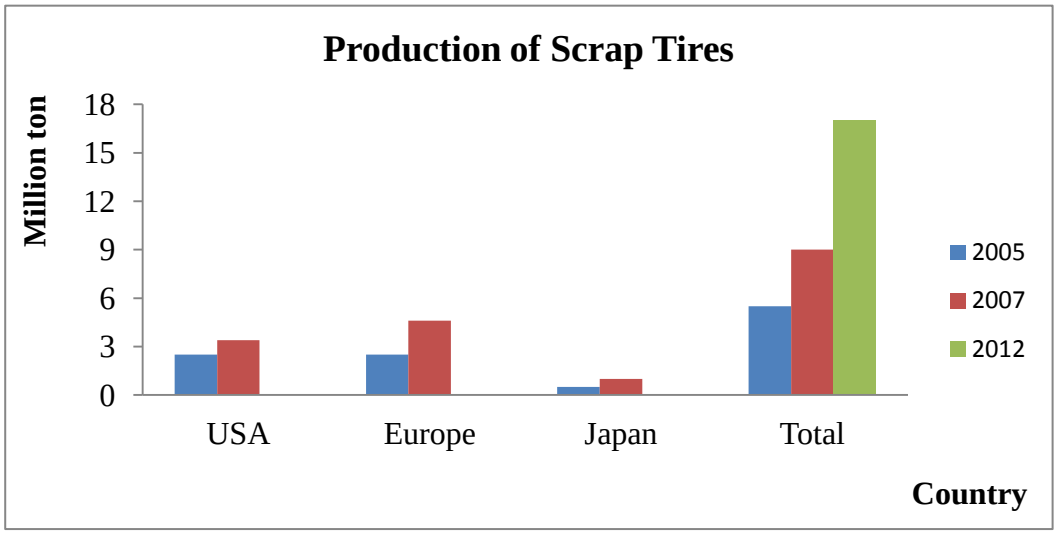


Figure 1-1, waste tire production

Although scrap tires account for only 2 wt% of total waste [5], their management is attracting growing interest in developed countries because of the environmental problems they may generate through inappropriate management, on the one hand, and the increasing demand for recycling raw materials, on the other.

European Union has introduced directives for the management of scrap tires including the European commission's landfill Directive (1999) which has banned the disposal of scrap tires to landfill since 2006 and the European End Life Vehicle Directive 2000 which requires that the 80% in weight of an end of life vehicle is recycled [8]. In other meaning, it proposes the following routine: to reduce, to reuse, to recycle, and finally, to perform an energy valorization process. Although it would be desirable to implement only the three first strategies, waste tire generation is so high that it is unavoidable to make use of energy valorization process.

In Europe, the main methods for scrap tires management are materials recovery (38.7%), energy recovery (32.3%) or retreading (11.3%) [9]. But globally, wide spread in the world, approximately 64% of used tires went to landfill or were illegally dumped or stockpiled, while only 13% were recycled [9].

Natural Rubber (NR), Styrene-Butadiene Rubber (SBR) and Butadiene Rubber (BR) are the most common rubbers used for tires. Sulfur is used to vulcanizing, steel and carbon black are used as reinforcing agents and aromatic extender oil is used to soften and enhance the workability of rubber. All of these components are 100% recyclable.

Tires are built to be tough and durable, the properties that ensure a safe ride and long service life, make scrap tire disposal a difficult task. Scrap tires are recalcitrant to natural degradation. The vulcanized rubber consists of long chain polymers (Polyisoprene = Natural Rubber, Polybutadiene, and Styrene-Butadiene copolymers) that are cross-linked with sulfur bonds and are further protected by antioxidants and antiozonants that resist degradation. Combustion of tires produces toxic gases which contain carcinogenic and mutagenic chemicals. So tires incineration requires expensive air emission control system [9].

Its approximate and ultimate analyses are showed in Table -1-1

Approximate analysis (wt %)		**Ultimate analysis (wt %)**		**remarks**
volatile	61-65	C	80 - 86	❖ Depends on ref 2,6,8, 10, 11 ❖ Others calculated by difference
Fixed carbon	31 - 33	H	6 - 9	
Ash	4 - 7	N	0.5 – 0.8	
Moisture	0.7-0.9	S	1 - 2	
GCV (KJ/Kg)	33-39	Others (O + ash)	9 - 20	

Table-1-1 approximate and ultimate analysis of scrap tires.

Scrap tires' high volatile, high fixed carbon , moderate sulfur and low-ash content with a calorific value greater than that of coal or biomass(max 30 MJ/Kg) make it an ideal material for thermochemical treatments (combustion, pyrolysis and gasification). High GCV is due to high carbon and hydrogen content.

Williams et al [8] says hydrogen is seen as a key future fuel to mitigate the consequences of climate change. 95% of current production is from fossil fuel. The use of waste materials as a source of hydrogen is particularly of interest in that it would also solve a waste treatment problem.

Scrap tires suppose a special challenge for their disposal or reuse because of their size, shape and physiochemical properties.

With the increasing emphasis on recovery and recycling of waste through the world, there is increasing interest in the development of new technologies.

1-II Material recycling and energy recovery technologies

The success of any tire-processing technology depends on environmental performance (emission) and process economics. The two most important factors affecting process economics are the tipping fees charged for tires disposal and the selling prices of products. Marek et al [2], advises to add other solid waste, *which capable to be pyrolysed like plastic and paper*, to tires pyrolysis, this will improve the economical revenue of the plant. Although a fair number of concepts and processes have been introduced, none is able to solve the problem on its own. Depending on existing technological facilities, environmental legislation, availability of money for environmental activities and public awareness, some of these concepts were successful to a certain extent.

1-II.1 Material recycling/reusing

1-II.1.1 Alternative applications (low value products)

The properties of used tires - elasticity of material, non-decomposable, inert - have led to a number of alternative applications like:

- In agriculture : as weights for silage cover sheets.
- In landscaping: as erosion protection for dam walls and slopes.
- In shore protection: as breakwaters.
- In harbors and docks: as dock bumpers and ship fenders.
- In the fishing industry: as artificial reefs for fish breeding.
- In household and communities: as bumpers in garages, playground equipment.
- Shoemaking: soles, heels and straps of sandals can be made from tire materials.
- Road construction: tires are mixed with asphalt cement forming asphalt rubber, asphalt rubber filler costs 40% more than conventional material [2].

It is obvious that these useful applications for scrap tires can only offer a limited outlet for the millions of old tires generated every year in a country. 2.5% of scrap tires are used in Germany for these types of applications [2].

1-II.1.2. Retreading of used tires

Retreading of used tires is the most preferable way of making use of old tires. On average only 15% of crude oil is needed to produce a retread instead of a new tire [10]. Thus, the price of a tire is reduced up to 45% without any loss in quality. But, tire for passenger cars normally are retreaded once, tires for Lorries are retreaded twice and aeroplane tires even up to seven times. In Germany, 12% of all passenger cars, 20% of all low duty vehicle LDV and 48% of all Lorries use retreaded, and 90% of the world's airlines use retreaded tires. That is on one hand, but on the other hands, there are two aspects, might be of negative impact on this process, which are:

- The acceptance of retreads by the customers: people tend to think that retreads are of minor quality compared to new tires. In spite of all investigations have shown that the retreaded tires have the same quality as the new tires. And some German manufacturers of retreads give 2 years guaranty on their products and allow their tires to be driven up to 190 Km/h [10].
- The availability of enough old tire of high quality: in countries where tires are valuable products compared to the average income, people want to drive a tire as long as possible, then tires are often driven until the threads or other internal layers become visible. These tires are of no use for retreading [10].

In this case we can see that retreading process solve the problem partially and it could not be applied always.

However, these measures - alternative application and retreading - are not capable of dealing with the massive numbers of scrap tires being produced.

Thermal valorization is emerging as a possible solution for reprocessing huge amounts of this material. The three main technologies for thermal valorization are: Pyrolysis, Gasification and Combustion.

- Pyrolysis : Thermal degradation in absence of oxygen.
- Combustion: Thermal degradation in presence of oxygen.
- Gasification: Thermal degradation in presence of gasification agent (water vapor stream, air…etc.).

1-II.2 Energy recovery technologies

1-II.2.1 Co-refining with crude oil

Scrap tires are added to the hot residue, (300°C-350°C), of the distillation column for crude oil and is depolymerized. The products resulting from the thermal cracking combined with the dense and less volatile fractions of crude oil follow the normal refining route. This process needs more research and studies for economy raison [10].

1-II.2.2 Incineration

Scrap tires are directly incinerated in appropriate energy-from-waste plants in suitable combustible chamber. The tires are either burned together with ordinary household waste or fed into special waste tire incinerators. The most applicable methods of this incineration could be in two cases:

1- Incineration in electricity power plant: for example, at a 14 MW power plant in Modesto, California, over 5 million of tires are incinerated every year producing 60 tons of stream of 65 bar and 500°C; providing enough energy for 15000 homes [10].
2- Incineration in cement kilns: tires are fed to the furnace as a whole or as shredded parts at the feed side of the furnace. The high combustion

temperature of up to 200°C and high oxygen potential in the combustion air guarantee a total combustion of the tires with only very little generation of dioxins and furanes. The off-gas cleaning system of the cement plant is not affected by using tires as additional fuel. In Germany, used tires make up to 15% of the total fuel for cement production [10].

Since scrap tires are a very homogenous feed without any fluctuation in composition, waste tire incinerators have the advantage of easy handling. The residue of this type of operation is very homogenous and marketable. The incinerator slag could be used in the steel industry, for road construction, or at least by landfilled without any problems. However, because of the elevated emissions of polyaromatic hydrocarbons (PAHs), NO_x, SO_2 and of heavy metals (e.g. zinc); expensive gas cleaning systems have to be installed in order to perform this process in an environmentally responsible fashion. In other words, combustion of tires produces toxic gases which contain carcinogenic and mutagenic chemicals. So tires incineration requires expensive air emission control system [9].

1-II.2.3 Distillation

Heating to moderate temperature in a controlled atmosphere of low oxygen-content presents new perspectives for upgrading waste of scrap tires. In Spain, for example, a pre-industrial plant has been built with a capacity of 1000 tons/year.

1-II.2.4 Gasification

Gasification is a thermal process, ($T \geq 750°C$) [11], that it allows converting carbonaceous materials, such as organic waste or biomass into carbon monoxide and hydrogen with a controlled amount of oxygen or steam. The resulting gas mixture, also called synthesis gas or syngas, is a full able to power gas turbines or fuel cells. This process is applied specially on the resulted char of the pyrolysis process. In another way, gasification is considered as second stage after pyrolysis.

It is possible to combine the two processes together under the name distillation-gasification technique. The yield of different fractions obtained, gas, liquid, solid, is similar to those reported in literature by means of pyrolysis in nitrogen atmosphere. One of the advantages of distillation-gasification is the simplicity of the technology and low investment cost [10].

1-II.2.5 Pyrolysis

One such recovery technologies is pyrolysis. Extensive studies on pyrolysis as a way to convert waste organic materials (oily sludge: residue inside the bottom of a fuel tank, fuel residue accumulates on the fuel filter, residue results from the purification lubricating oil, oily waste, organic materials in municipal waste: oil, soap, tires, plastic, textile…etc.) into useful products have been carried out for decades [7]. Pyrolysis of tires involves the thermal degradation of the rubber of the tire at temperature (300°C-900°C) in an inert atmosphere. The pyrolysis of scrap tire has received increasing attention since the process conditions may be optimized to produce high energy oil, gas and residual char in addition to the steel casing of tire. Steel is recycled back into iron or steel industry. The other three products are used as energy (fuel) or/and chemical resources [1, 8, 12].

In the pyrolysis process, the organic volatile matter of tires is decomposed to low molecular weight products, liquid or gases. The inorganic components and the non-volatile carbon black remain as a solid residue which is relatively unaltered, and therefore can be recycled in worthwhile applications.

Marco et al [10], indicated that pyrolysis process is especially appropriate for complex wastes, which contain many different plastics mixed with other materials (soil, textile, glass…etc.), as in the case of **A**utomobile **S**hredded **R**esidues (ASR), which does not need pre-cleaning process and the solid product could be used in the metaling manufacture and carbon black activation. If pre-cleaning process has been done, it is better to get higher quality solid residue but, this is less economic.

Pyrolysis process consists of exothermic primary cracking reactions, endothermic secondary cracking reactions and vaporization process. The endothermic processes dominate the energy requirement of pyrolysis process and

therefore, most of the pyrolysis processes are globally endothermic (Ka-Leung et al [3]).

1-II.2.5.1 Char/pyrolytic solid residue

Its yield and application depends upon the composition of raw materials and the conditions of pyrolysis process. By normal pyrolysis using shredded scrap tires, the yield is 35-40% *wt*, califoric value ≈ 30MJ.Kg^{-1}[1, 8, 12], and it is used as a reasonable source of solid fuel or has properties which may be suitable for its use as a low grade activated carbon or carbon black [8]. Another potentially end-use of the pyrolytic carbon black may be used as an additive for road bitumen [1, 8]. The char which was obtained by Marco et al [10], could be used for both application, steel and metal industry and activated carbon production.

The judgment of completed pyrolysis depends on the elemental analysis of char. For example if it still contains more hydrogen, that means the pyrolysis process is not completed and needs either more time of reaction or to raise up the temperature[12].

The pyrolytic char obtained by Jasmin et al [4], was treated with acid to remove the mineral from it, then it was activated at 900°C. The resulted active carbon was comparable with these available commercially in surface area and adsorption capacity. Activated carbon is widely used for water purification, air purification and also in batteries and fuel cells.

1-II.2.5.2 Pyrolytic oil

Up to 58% has been produced. It has broad fuel properties similar to commercial grade light fuel [8] (Table 1-2). ^{1}NMR, GC, GC-MS, FT-IR analytical techniques showed that its composition consists of a wide range of chemicals with a wide range of molecular weights (mixture of paraffins, olefins and aromatic compounds). Its high gross calorific value (GCV) of around 41-44 MJ/Kg [1, 12] which encourage its use as replacements for conventional liquid fuels [1]. In addition to its use as fuel, the pyrolytic oil showed that it is a potential source of light aromatics

such as benzene, toluene and Xylene (BTX), which command a higher market value than the raw oils. Similarly, it has been shown that pyrolytic oil also contains monoterpene such as limonene, a high value light hydrocarbon, limonene has extremely fast growing and wide industrial applications including formulation of industrial solvents, resins and adhesives, as a dispersing agent for pigments, as a fragrance in cleaning products and as an environmentally acceptable solvent. Limonene is very common in cosmetic products and also used as flaming combustible liquid. The presence of aromatic compounds in the pyrolytic oil is due to, on the one hand to the aromatic nature of the source polymeric materials, and on the other hand, to recombination reactions that take place among aliphatic and aromatic fragments and also to cyclization of aliphatic chains followed by dehydration reactions, which take place during the pyrolysis processes.

Also, pyrolytic oil can be stored until required or readily transportation to where it can be most efficiently utilized [1].

Elements	**Pyrolytic oil %**	**Diesel %**	**Physical properties**	**Pyrolytic oil**	**Diesel**
C	86.52	84-87	Density (kg/m3)	943	820-860
H	9.35	12.8-15.7	Viscosity(cSt)	4.62	2-4.5
N	0.53	<3000 ppm	Flash point (°C)	≤30	>55
S	1.30	<7000 ppm	Pour point(°C)	- 4	(-40) – (-30)
Ash	0.2	0.0	Water (wt%)	N/A	≈80 ppm
O	2.10	0.0	pH value	4.30	-
H/C	1.30	1.76-2.24	GCV MJ/kg	41.60	44-46

Table 1-2, Comparing between pyrolytic oil and fossil one.

- Density of pyrolytic oil is higher than that of the commercial diesel fuel but lower than that of heavy fuel oil (980 kg/m^3 at 20°C).
- The viscosity of pyrolytic oil is slightly higher than that of the diesel but too much lower than that of heavy fuel oil (200 at 50°C).

- Refining the pyrolytic oil could change these properties.

Pyrolytic oil requires preliminary treatments such as decanting, centrifugation, filtration, desulphurization and hydro-treating before to be used as fuels directly (industrial furnace, power plant, boiler.) or by blending with fossil diesel.

The tire pyrolysis liquids production pathway with their wide range of potential opportunities for heat, chemicals, fuels and electricity applications are indicated in fig.1- 2.

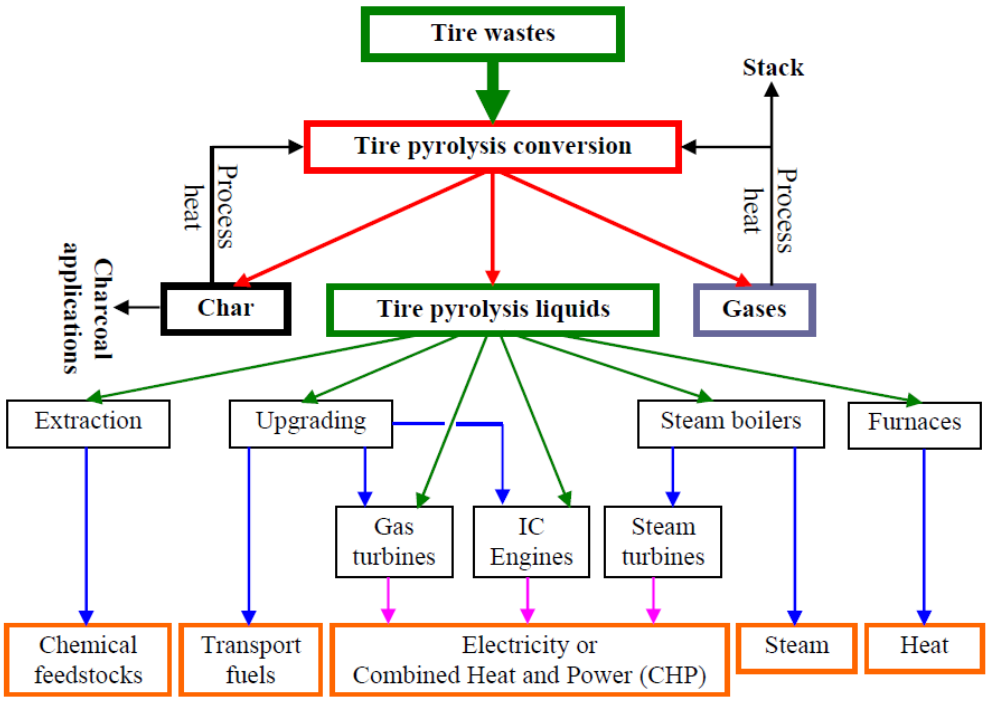


Figure 1-2-: Tire pyrolysis conversion and applications of products.

1-II.2.5.3 Pyrolytic Gas

Composed mainly of hydrogen, methane and other hydrocarbons C_1-C_4, in addition, it is possible to find some CO and CO_2, these gases come from the oxygenated polymers of the tires (polyesters, polycarbonates…) and even come from inorganic matter such as carbonate fillers.

Pyrolytic gas has sufficient GCV of approximately 37 MJ/m^3 [1, 12], in comparison with natural gas which has 35 MJ/m^3 [3], therefore the pyrolytic gas is successfully employed as fuel, especially for producing electricity, or, at least it can provide the energy requirements for the pyrolysis process [1, 8, 12].

Pyrolytic gas is calculated by difference between the pyrolysed sample weight and the weight of both char and oil.

The pyrolytic products: char, oil and gas vary drastically in composition depending on the composition of raw materials and on the pyrolysis conditions.

Very different experimental procedures have been used to obtain liquid products from automotive tires wastes by pyrolysis technology including fixed-bed reactor, fluidized-bed pyrolysis unites, vacuum pyrolysis unites, spouted-bed reactors, etc.

1-II.2.6 Other Pyrolysis Techniques

1-II.2.6.1 Catalytic pyrolysis

Catalytic pyrolysis has been used to enhance the concentration of higher value chemicals in the oil and produce oil which can be used as a chemical feedstock rather than fuel [8] (limonene, benzene, toluene, etc). NaOH, CaCO3, MgO, Zeolite are the most famous used catalysts. NaOH, for example, can promote the rapid cracking of organic compounds scrap tires rubber into small molecular compounds, even at low temperatures [1].

As well, Ni-Mg-Al catalyst was used by Williams et al [8], to increase the yield of gas product from 22% without catalyst into 43% with catalyst, and the H_2 concentration, as well, in the gas product was changed from 26% into 67% in respect.

1-II.2.6.2 Vacuum pyrolysis

Vacuum pyrolysis of scrap tires was developed by C. Roy [13], and a series of studies has been conducted (Pakdel et al [14]) To date, a pilot plant with scrap tire input of 15-20 t/h has been established by the C. Roy group. Vacuum pyrolysis had some advantages compared with atmospheric pyrolysis. First, the residence time in the reactor was shorter, which reduced undesirable reactions. Secondly, the yield of pyrolysis oil was higher. Thirdly, the concentration of aromatic chemicals in the pyrolysis oil was higher, which enhanced the octane value.

On other hand, the content of naphtha (low boiling point fraction) in the pyrolytic oil is low, because the volatile vapors were evacuated from the pyrolysis reactor by a vacuum pump, which prevent the secondary cracking of volatile vapors. Thus, the condensed pyrolysis oil was mainly composed of compounds with a high boiling point, and the content of naphtha in pyrolytic oil was small [6].

At low pyrolysis temperature, the oil was mainly composed of small molecule compounds with low boiling points. As a result, the content of naphtha in pyrolytic oil was higher, but the yield of pyrolytic oil was very low and thus the total yield of naphtha would be rather low – a factor which should be considered. In general, the content of naphtha in the pyrolysis oil obtained under vacuum conditions was lower than that obtained under atmospheric pressure. And the percentage of limonene in naphtha is the highest which has high economic value and extensive applications, so market demand for limonene has increased rapidly.

1-II.2.6.3 Thermal Plasma Pyrolysis Technology

Plasma is considered by many to be the fourth state of matter, following, the more familiar states of solid, liquid and gas. Addition of sufficient energy to a gas converts the gas into plasma. In other words, plasma is an ionized gas resulting from an electrical discharge, for instance. Thermal plasma pyrolysis can be described as the process of reacting a carbonaceous solid with limited amounts of oxygen at high temperature (10000°C $\geq$ T $\geq$ 5000°C)[15, 11] to produce combustible gas, having a calorific value in the range of 4-9 MJ/Nm^3, and

carbonaceous solid products, no liquid product [15]. In the highly reactive plasma zone, there is a large fraction of electrons, ions and excited molecules together with the high energy radiation. When carbonaceous particles are injected into plasma, they are heated very rapidly by the plasma; and the volatile matter is released and cracked giving rise to hydrogen and a light hydrocarbons such as methane and acetylene. High temperature combined with the high heating rate of the plasma results in the destruction of organic waste, giving rise to a gas and a solid residue with varied properties depending on the feed characteristics and operating conditions. The amount of gas product can reach up to 70-80% of the feed, for comparison, the gaseous product generated by conventional pyrolysis of scrap tires is only 10-20% for slow pyrolysis and 30-50% for rapid pyrolysis. The heating value of the gas product is in the range of 4-9 MJ/Nm^3, so it can be used directly as a fuel in various energy applications such as direct firing in boilers, gas turbines or gas engines. Heating values of the chars obtained from plasma pyrolysis are usually comparable with those of lignite and coke and can be used as a solid fuel directly.

Thermal plasma reactors need significant amounts of energy input to achieve their high processing temperatures. This makes them costly to operate. However, when the energy content of the pyrolysis products is utilized and recycled, the plasma pyrolysis treatment process is energy self-sufficient, so the operating cost is significantly reduced. Plasma pyrolysis has the following advantages:

- Efficient delivery of heat energy for simultaneous rapid promotion of both physical and chemical changes in waste material.
- Easy achievement of high and effective processing temperatures in very compact, high throughput and fast response reactors.
- The properties of plasma pyrolysis products are suitable for energy and material recycling.
- Non-polluting and capable of destroying substances harmful to human health, and the products are predictable, harmless and acceptable for public health and environment.

1-III Parameters of pyrolysis

The yield and composition of each pyrolytic product (char, liquid and gas) is affected by the conditions of the pyrolysis process.

1-III.1 Reactor temperature

M. Rofiqul et al [1], found that the rubber tire starts to decompose at 375°C that the solid starts to decrease and both gas and liquid start to increase until 475°C, then, above 475°C, the yields of both liquid and gas decreases and increases respectively, it is due to the decompose of some oil vapor into permanent gases.

I. de Marco et al [10], found that 500°C is the optimum for pyrolytic oil products and the increasing temperature over 500°C increases gas yield to the detriment of liquid, but hardly varies the characteristics of the products. In addition, there is no decrease in the solid yield that means the pyrolysis process is completed.

The pyrolysis was achieved under three different temperature which are 600°C, 700°C and 800°C [16], with fixed other parameters like reactor design, flow rate, mass flow rate. The result was that the produced solid contents the same leaving the volatile matter < 5%. The solid yield is constant (≈ 40%). But the gas fraction increases (from 17% into 31.5%) and therefore the liquid fraction decreases (from 41.5% into 27.5%) when the temperature reaction is increased. This could be mainly due to the severe cracking of the primary pyrolysis products occurring at higher temperatures. The effects are also appeared in the increasing percentage of low boiling materials in the liquid fraction. This result could be changed depending on other parameters like (reactor design, raw material composition, heating flow rate…etc).

Temperature increasing promotes the formation and percentage increasing (13.1wt% at 425°C to 22.9wt% at 600°C) of C_{10} aromatic compounds from olefin due to Diels-alder reaction [5]. In contrast, the percentage of non-aromatic C_5-C_{10} decreases, due to thermal cracking and secondary reactions at high temperature.

The pyrolysis's products yields were changed drastically when the temperature was changed from 400°C (solid: liquid: gas 85:10:5) into 500°C (solid: liquid: gas 55:35:10) Sermin et al [7].

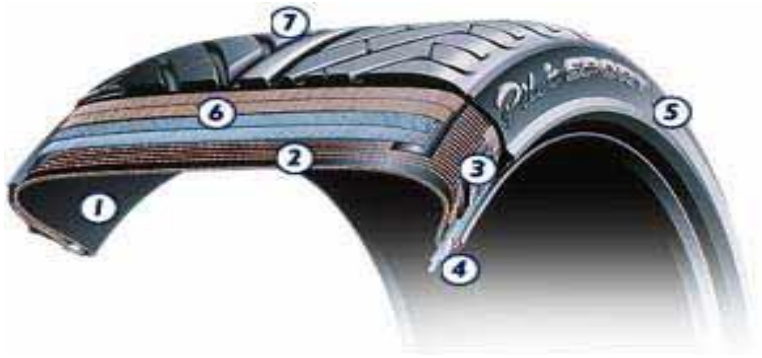
1-III.2 Particle size of feedstocks

M. Rofiqul et al [1], studied the effect of changing particle size on the yield of pyrolytic oil under fixed applied others conditions, temperature at 475°C, residence time 5 second. They found that with increase the particle size from 2 cm^3 to 12 cm^3, the pyrolytic oil yield increases until the particle size is 4 cm^3 with 51%, after that the yield decreases. They concluded that smaller particle size provides more reaction surface causes high heating rate and too quick decomposition of the rubber. On the other hand, the heating rate in large particle size is low due to its lower thermal conductivity and heat can flow only to a certain depth in the available pyrolysis time compared to almost complete thermal decomposition of the smaller pieces. Thus the core of the larger pieces become carbonized and/or can't be decomposed completely resulting in an increase in char and a decrease in liquid and gas yields.

As pyrolysis is limited by heat and mass transfer within the particle, and consequently, as particle size is decreased, the apparent kinetic constant increases. Gartzen et al [12], found that 1mm particle size is suitable for continuous pyrolysis, bed stability and the removal of adultered carbon back. On another hand, smaller particle size requires more energy for grinding and the kinetic is not affected when smaller sizes are used.

Xinghau et al [6], used 20-60 mesh range of particle size. They obtained higher yield of dl-limonene.

As the tire is consisted of different heterogeneous layers; figure 1-3, the pyrolysed sample should represent the whole tire, so it is mixed well and get very fin and small portions.



1. A rubber sheet
Synthetic very airtight
2. Water-frame.
3. Lower area jam
4. rods
5. sides
6. Tablecloths-summits
7. Tread

Figure 1-3, Tire composition.

1-III.3 Solid residence time (reaction time)

It is an important variable in the pyrolysis process; its optimization is a key factor in order to scale up an industrial system. Lower residence times involve lower reactor volumes to process a certain load of tire and, therefore, lower cost of the system [16]. The variation of the solid residence time involves the variation of the gas residence time. This variation is due to the increment of the free volume inside the reactor.

1-III.4 Residence time/inert gas flow

M. Rofiqul et al [1], studied the effect of residence time of the vapor in the reactor on gas, char and liquid yields for optimum reactor temperature and for optimum feed size. They arrived to this conclusion; when the flow rate of N_2 is increased, consequently the vapor residence time inversely decreased, increased the rate of removal of pyrolysis vapor products from the hot zone. Then the gas and char yields decrease while the liquid yield increases slightly. But with increase the residence time, it also help to the decomposition of some oil vapor into secondary permanent gases, which leads to less oil and more gases products. In addition, long

contact time between the volatiles and the char leads to another parallel secondary pyrolysis reaction and hence reduces in volatiles' yields. The increase of the gas residence time would favor the cracking of the primary pyrolysis products and would promote a change in the gas: liquid ratio. Nevertheless, it has been considered that higher percentage of nitrogen in the final gas would suppose an excessive dilution of gas fraction and therefore these gases may not have enough calorific value to satisfy the process requirement.

1-III.5 Design of reactor

Different technologies are reported in the literature for tire pyrolysis. Fixed bed reactors have been commonly used, in which temperature is increased following a ramp until a final temperature is reached. Furthermore, other authors have operated under isothermal conditions by feeding the tire when the reactor is at reaction conditions.

Another successful technology applied in the tire pyrolysis process is that based on the rotary kiln. Fluid bed reactors have been used especially for their high heat transfer and bed isothermicity.

The conical spouted bed reactor has been successfully used for both tire pyrolysis and, previously, in the pyrolysis of other residues, such as biomass and plastics.

The conical spouted bed reactor is of easy design, given that it does not require a distributor plate, and has low pressure drop. As shown in figure 1- 4.

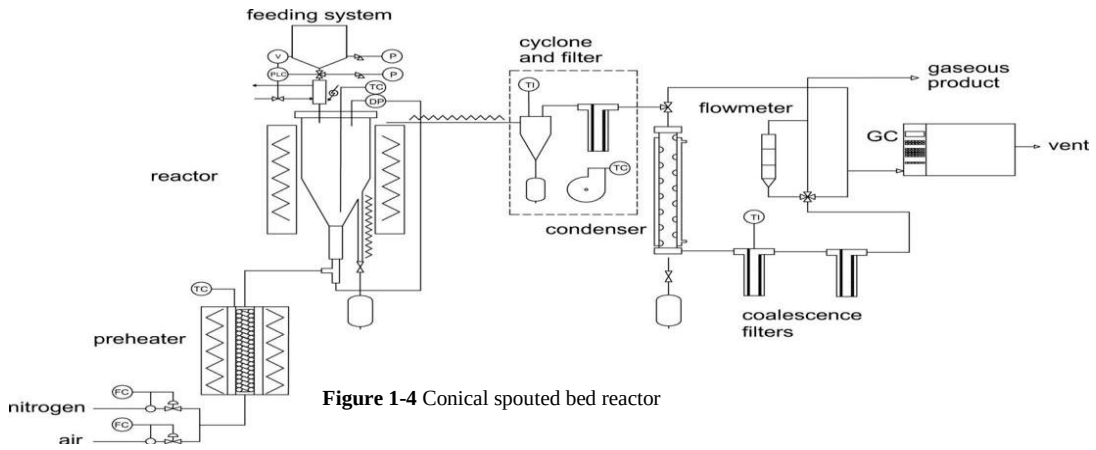


Figure 1-4 Conical spouted bed reactor

In addition, the conical geometry of the reactor makes the bed extremely versatile for operation with high gas velocities and consequently, a vigorous gas-solid contact is generated, which enhances heat and mass transfer between phases, increasing the heating rate of the solid and avoids bed defluidization by agglomeration of particles, even under severe conditions involving very sticky particles. Furthermore, the conical spouted bed reactor is suitable for continuous operation, which is especially relevant for the implementation of tire pyrolysis at large scale.

Xinghau et al [6], used stainless steel reactor with an inner diameter of 32 mm and a depth of 120mm, figure 1-5. Several stainless steel plates were fixed inside the reactor to strengthen heat transfer, the heating rate was 20°C/min and under vacuum of 3.5-10 kPa. The condensation process of the volatile produced materials contains two steps. At first by cooling water then the uncondensed vapor was condensed further by four cold traps with water-ice-sodium chloride.

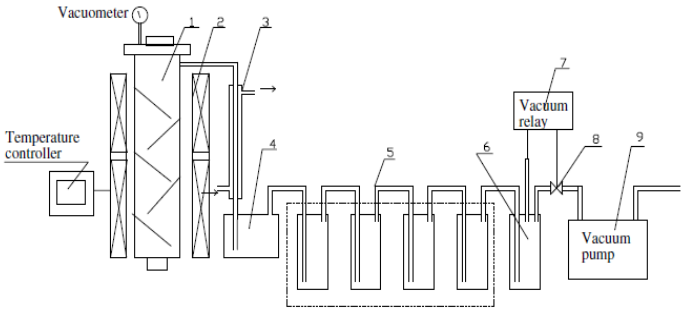


Figure 1-5. Stainless steel reactor with plates. (1) Pyrolysis reactor, (2) Electrical furnace, (3) Primary condenser, (4) Liquid collector, (5) Secondary collector, (6) Safe-buffer, (7) Vacuum relay, (8) Electromagnitic valve, and (9) vacuum pump. [6].

51% pyrolytic oil was obtained by M. Rofiqul et al [1], using a fixed-bed fire-tube internal heating reactor chamber, a gravity feed type reactor feeder, two ice-cooled condensers, a N_2 gas cylinder, N_2 gas pre-heater, an air compressor, char collection bag and thermocouples. At a distance of 30 mm from the closed bottom of the reactor, a distributor plate was fitted to support the feedstock. Eight equally spaced stainless steel, 10mm diameter fire-tubes containing insulated electric coil of a total capacity 1.60 kW were fixed inside the reactor. The fire-tube and

preheated N_2 gas provided uniform heating across the cross-section of the reactor chamber. Fig1-6.

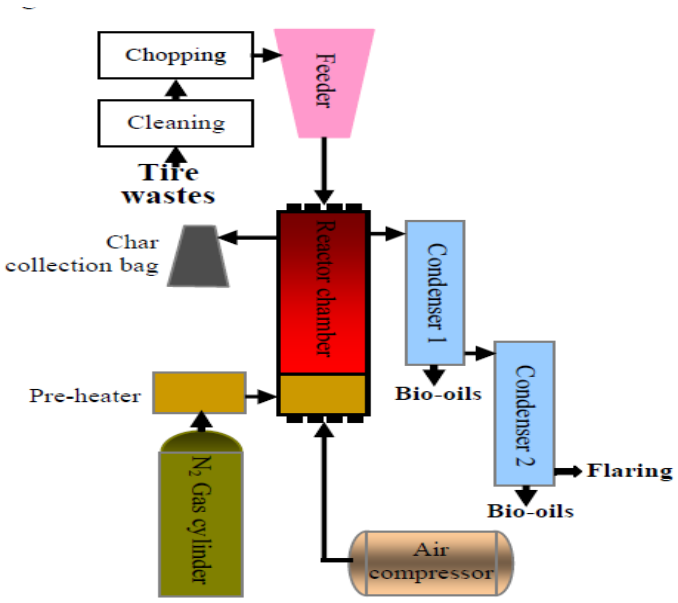


Figure 1- 6. Fixed-bed fire-tube heating pyrolysis system [1].

Williams et al [8], used another type of reactor, it consists of two stages reactor, the first for pyrolysis at 500°C and the second stage is for steam gasification or catalytic steam gasification at 800°C as shown in fig 1-7. This type of reactor is used to get high revenue of hydrogen as a final product. Hydrogen is considered as a clean energy fuel since the product of hydrogen combustion is only water with consequent mitigation of climate change impact of the use of fossil fuel combustion and would reduce the worlds depending on fossil fuel.

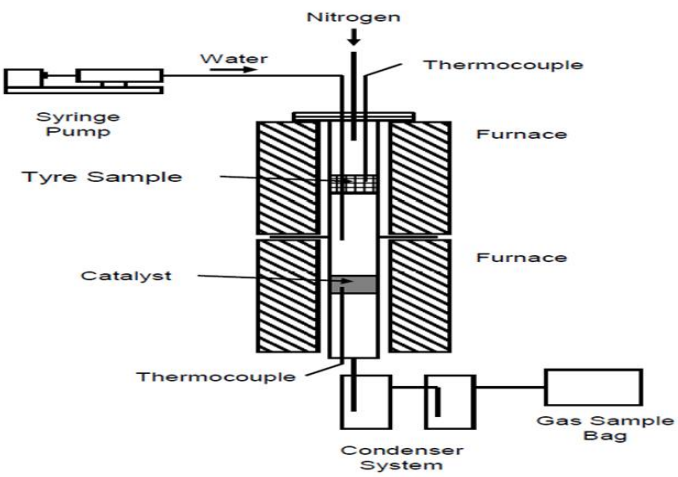


Figure 1-7. Two stages reactor [8].

1-III.6 Mass flow rate

This variable affects considerably the gas/liquid ratio while the solid yield remains constant. The higher the mass flow rate, the lower the free volume inside the reactor and, on the other hand, as a consequence of a higher mass flow rate, there is an important increment in the volatile matter released. Both effects make the gas residence time inside the reactor decrease considerably. This remarkable decrease of the gas residence time when mass flow rate is increased, limits the cracking of the gas fraction; therefore a bigger amount of liquid is obtained in the process [16]. This effect can be observed also in the product characterization. When the mass flow rate is increased, the gas fraction obtained presents a higher percentage of the heaviest compounds.

1-III.7 Catalyst

Sermin et al [7], pyrolysed individual scrap tires (ST) , oily sludge (OS), bilge water oil (BW) and a mix of (OS:BW:ST 1:1:2) in presence/absence of catalysts. The used catalyst were FCC (fluid catalytical cracking used in refinery, commercial catalyst) and RM (Red Mud, disposal catalyst) with ratio 1:5 (catalyst: feedstock) mass rate. The catalysts were laid between two layers of quartz wool in a stainless-steel net basket that was placed in the middle part of the reactor, being in contact with the gaseous products from primary degradation of materials. This method of using catalyst due to the expectation for the contaminants in waste materials to poison the catalysts making their regeneration difficult and less effective. The result showed that the catalysts didn’t have significant effects on the yields of both gas and liquid products for the pyrolysis of scrap tires. But they had big effect on the composition of liquid ex: the percentage of paraffins changed from 65.6 to 51.3 for RM catalyst, and the percentage of aromatics changed from 13.9% into 18.4% for FCC.

1-IV Mechanism of pyrolysis

In order to design tires pyrolysis, it is helpful to know the kinetics of thermal decomposition of tires. The decomposition of the organic part of tires can be related to the decomposition of its separate components [24] (extender oil, natural rubber…). That is reflected in variation in activation energy of pyrolysis process when the tire's composition is different, in addition to the variation in the parameters (heating range, temperature…) of process itself. Sylvie et al [17], assumed that the reaction rates follow first order kinetics, which is a reasonable assumption for the polymers used in tires. They used T_{max} method to determine the activation energy E_a and the pre-exponential factor A depending on the following equation:

$$\ln(M/T_{max}^2) = \ln(AR/E) - (E/RT_{max})$$

Where M is heating rate and T_{max} is the temperature at which the rate of volatile evolution is maximum in degrees Kelvin. By plotting the term $\ln(M/T_{max}^2)$ as a function of the inverse temperature $(1/T_{max})$. There are two drawbacks in this method:

1. In such cases, substantial shifts in T_{max} can occur, when peaks are not well resolved.
2. The assumption of first order kinetics is not fully supported.

These limitations can be resolved by:

1. Large number of heating rates.
2. Very low heating rates for the improved peak resolution.
3. In the case of noisy data, the measurement of T_{max} was made at the mid-point of the peak width in order to minimize the effect of noise on T_{max}.

1-V Literature study, results of some researchers

In order to exploit pyrolysis process as a potential technology for energy and raw materials recovery from scrap tires, several laboratories and pilot scale projects have been undertaken in different countries. And a number of studies have been reported in literature related to tires pyrolysis for its conversion into valuable compounds.

The pyrolysis and gasification of scrap tires for the production of liquid fuels, chemicals feedstocks, activated carbons and gases has been extensively researched.

Williams et al [8] investigated the production of hydrogen and other gases from the bench scale pyrolysis-gasification of scrap tires. The experiment was carried using two stages system consisting of pyrolysis of the scrap tires at 500°C followed by catalytic steam gasification in a second reactor at 800°C using Ni-Mg-Al (molar ration 1:1:1) as catalyst. They did three experiments: pyrolysis, pyrolysis-gasification with steam and pyrolysis with catalytic steam gasification the results are shown in the table1-3.

Product	Pyrolysis	Steam gasification	Catalytic steam gasification
Gas %	22.2	26.5	43.1
Solid %	36.7	32.8	49.5
Oil %	33.0	42.6	20.3
Mass balance %	91.9	102.0*	112.9*

Table 1-3, Product yield from pyrolysis, pyrolysis-steam gasification and pyrolysis-catalytic steam gasification of scrap tires [8]. *Include the reactant water from the stream and also the formation of CO and CO_2 from the stream

The pyrolysis oil is subject to secondary cracking reactions, leading to an increase in the gas yield and decrease in oil yield. Gas composition related to process conditions as shown in the table 1-4.

Product	Pyrolysis	Steam gasification	Catalytic steam gasification
H_2 (vol %)	21.9	24.62	66.69
CO (vol %)	0	3.24	16.01
CO_2 (vol %)	0	3.76	5.29
CH_4 (vol %)	44.3	37.26	8.73
C_2-C_4 (vol %)	33.8	31.09	3.28
Hydrogen production (wt%)	0.52	0.68	5.43

Table1-4, Gas composition and hydrogen production in the produced gases from pyrolysis, pyrolysis-steam gasification and pyrolysis-catalytic steam gasification of scrap tires [8].

1- The reacted catalyst Ni-Mg-AL was deposited with large amounts of filamentous carbons 31%wt.
2- The reactor is bed reactor shown in the figure 1-7.

M. Rofiqul et al [1], studied the pyrolysis of waste tires in an internal heated fixed-bed fire-tubing heating reactor system under N_2 atmosphere (cf. Fig.1-6) and investigated the effects of operating temperature, feed size and vapor residence time on the yields and compositions of product liquids. The highest pyrolytic oil product yield (51%) was obtained at a pyrolysis temperature of 475°C for size of 4cm^3 and vapor residence time of 5 sec, with yield solid char 40.5%wt and gas 8.5%wt. The liquid composition was consisted of C_5-C_{16} organic compounds, a lot of high value light hydrocarbon limonene, single ring alkyl-aromatics and long-chain hydrocarbon.

I. de Marco et al [10], used the rejected (heterogeneous) automobile shredder residues (ASR) of a metal recovery of end-of-life vehicles plant, which are composed of several plastics, foam, glass, rubbers, textiles, remaining metals, soil… etc., to recover the gas and liquid (as a source of fuel and chemical) by the pyrolysis technique. They used two kinds of ASR light, lighter fraction separated from the total product shredded in a first step by simple suction, and heavy, which left after ferrous metals that are magnetically removed from the non-sucked stream.

They carried out the experiments in non-stirred batch 3.5 dcm^3 autoclave , 100g sample size , heating rate is 15°C/min, temperatures 400°C, 500°C and 700°C for 30 min, in nitrogen atmosphere. The results were valuable amounts of solid (38-39 % wt), liquid (20-29%) and gas (31-41%) of heavy ASR at 500°C, while the case was less valuable with light ASR (58.5-69.4% solid, 7.1-8.8% liquid and 23-33% gas). They judged that at 500°C, the pyrolysis process is finished because with increasing temperature to 700, there was no decrease in the solid yield.

Ka-Leung et al [3], took into account the thermal behavior of pyrolysis by proposing multi-stages pyrolysis as an approach to optimize waste tire pyrolysis process by minimizing the pyrolysis energy requirement. They used a tire particle with radius of 3 cm in a batch reactor that can provide a constant heating rate of 10°C/min and target pyrolysis temperature of 510°C in nitrogen atmosphere.

At first, Ka-Leung et al models the experimental results from the thermo-gravimetric analysis and differential thermal analysis to obtain the parameters of both tire pyrolysis kinetics and heat transfer. The parameters were then used to build a tire particle pyrolysis model that describes the mass loss and heat transfer phenomena of single tire particle pyrolysis. This model was used as the basis for making comparison between conventional pyrolysis approach and the proposed multi-stage pyrolysis approach.

They considered the mass loss reaction is endothermic reaction and they used thermo-gravimetric analysis results to determine the parameters of mass loss kinetics. While, differential thermal analysis results were used to determine the kinetic parameters of exothermic cracking reactions. In the proposed model, it is assumed that the tire particles is spherical and is heated up by pyrolysis gas by convection inside the reactor while heat is transferred inside the particle by conduction only. In the reactor, the temperature is assumed to be the same as the pyrolysis gas temperature. The heat balance can be described in terms of the particle temperature change across the radius and time. In this way, the pyrolysis process is divided into several heating stages to reduce the overall process heat requirement and to provide a better control of products' yield and quality. In this way, they save about 21.7% of energy compares to the conventional approach.

Jasmin SHAH et al [4], used pyrolysis process to obtain activated black carbon after treatment with acid (for demineralization, decrease of inorganic impurities as well as to remove undesirable ash contents) and activation at 900°C. The pyrolysis was achieved at 450°C under atmospheric pressure in a batch reactor of glass tube and feedstock of 10 g, with heating rate of 20°C and 2 hours reaction time. The obtained activated carbon was similar to that one available commercially in comparison with surface area 990 m^2g^{-1}/ 800-1100 m^2g^{-1}, elemental analysis and adsorption capacity of methylene blue.

The influence of the main pyrolysis process variables (temperature, solid residence time, mass flow rate and inert gas flow) has been studied by E. Aylon et al [5]. Using a moving bed reactor designed to process up to 15 kg/h of scrap tire, it has been proven that, in the studied range, the most influencing process variables are temperature and solid mass flow rate, mainly because both variables modify the gas residence time inside the reactor. In addition, it has been found that the modification of these variables affect the chemical properties of the products. This fact is mainly associated to the different cracking reaction of the primary products.

Cartzen et al [12] carried out the pyrolysis of scrap tires continuously in a conical spouted bed reactor and the results (yields, composition of the volatile fraction and carbon black properties) have been compared with thus obtained operating in batch mode. This continuous operation in the 425-600°C range gives way to a yield 1.8-6.8 wt% gas, 44.5-55% liquid and 36-39% char. The main differences between continuous and batch processes are in the yield of light aromatics, which is higher in the continuous process, and in that of the heavy liquid fraction or tar, which is higher in the batch process. The conical spouted bed reactor performs in excellent way the tires pyrolysis due to the solid cyclic movement, the good contact between phases, the high heating rate and the reduced residence time of the volatile products.

Pyrolysis of scrap tires under vacuum (3.5-10 kPa) with and without basic additives (catalysts) was studied by Xinghau et al [6]. They found that with and without basic additives, pyrolysis oil yield increased gradually to a maximum and subsequently decreased with a temperature increase from 450°C to 600°C. The addition of NaOH facilitated pyrolysis dramatically, as a maximal pyrolysis oil

yield of about 48wt% was achieved at 550°C without the addition of basic additives, while a maximal pyrolysis oil yield of about 50 wt% by adding 3 wt% (w/w, powder catalyst/scrap tire granules) of NaOH powder. The composition analysis of pyrolytic oil showed that more dl-limonene was obtained with basic additives and the maximal content of dl-limonene in pyrolysis oil was 12.39 wt%, which is a valuable and widely-used fine chemical. However, no improvement in pyrolysis was observed with Na_2CO_3 addition. Pyrolytic gas was mainly composed of H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6. Pyrolytic char had a surface area comparable to commercial carbon black, but its proportion of ash (above 11.5 wt %) was much higher.

Distillation of scrap tires -at 550 ºC in the atmospheric pressure with controlled amount of oxygen- yielded tires derived oil (TDO), gas and distillation carbon black (DCB) with percentages of 46.2 ± 0.3, 13.8 ± 0.6 and 39.9 ± 0.8 (wt %) respectively. Then, DCB was gasified –under pressure of 15 atm, in the presence of steam- to produce very important and useful syngas (H_2 +CO) with yield of 97.5% [18]. This result reveals that *distillation and gasification* technique is viable for the treatment of the tires. The resulted syngas is directly used to support the process in one part and another part is directed straightly to electricity generation power plant.

Box-Wilson technique of experimental design with computer program called "optimization technique" have been used by Mahmood et al [17] to study the optimization of pyrolysis conditions of scrap tires under inert gas atmosphere. The yields of char and oil were 32.5 and 51.0 wt% respectively, under the following conditions: temperature 430°C, inert gas flow rate 0.35 m^3h^{-1} and particle size of 10 mm. in a fixed bed batch reactor heated by electric furnace. In addition, a quantitative relationship could be obtained between the experimental variables and the yield of either of the oil and the carbon black.

A comparison, of yield of tires pyrolysis in laboratory and pilot scales, was achieved by Adéla et al [20]. The results and the condition of work are presented in table 1-5:

work	Char %	Liquid %	Gas%	Conditions and remarks
Laboratory scale	39	44	16	• The difference to 100% is water and ash. • Heating rate 2.7°C/min, residence time 60 min, temperature range 175-600
Pilot scale	39.16	51.47	8.94	

Table 1-5. Result of different scale work of pyrolysis [20]

Fernandez et al [21] studied the pyrolysis of two kinds of scrap tires which are granulated rubber and textile fibers at two different temperatures 550°C and 900°C. The results are shown in table 1-6:

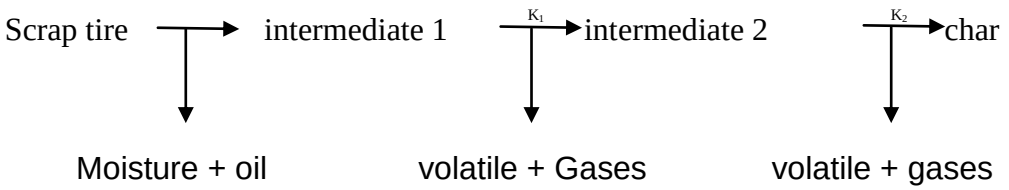
Work	Char % 550/900°C	Liquid % 550/900°C	Gas% 550/900°C
Granulated rubber	40/38	54/56	6/8
Textiles fibers	36/38	52/52	12/8

Table 1-6. Result of pyrolysis of different types of tires at different temperature [21].

With respect to the pyrolysis yields, 550°C was a high enough temperature for the pyrolysis of the tire since decomposition was completed and no significant differences were found in the solid, liquid and gas yields at higher temperature. The composition of the oil indicates that some compounds such as limonene are present in high amounts. In the case of the gas, the most abundant component was C_4.

The distribution ratio of solid: liquid: gas with MgO and $CaCO_3$ as catalysts were 35.8 : 39.8 : 24.4 wt% and 35.2 : 32.2 : 32.5 wt% respectively at 350°C for 2 hours catalytic pyrolysis in a batch reactor under atmospheric pressure [18]. Both catalysts produced 25 wt% of aliphatic hydrocarbons in liquid portion, but with the use of MgO the aromatic increased (55%) and polar hydrocarbon decreased (20%) as compared to $CaCO_3$ catalyst (50% aromatic and 25% polar hydrocarbons).

Kinetic parameters of scrap tire pyrolysis and combustion of derivate pyrolytic char was investigated by D.Y.C. Leug et al [22] using thermo-gravimetric (TG) and derivative thermo-gravimetric (DTG) analysis method. Thermal degradation models were proposed to derive the kinetic parameters. It was found that the process and kinetic parameters vary with heating rates but less dependent on the powder size. DTG curves show that there are three temperature regions of reaction (weight loss) between 150°C and 600°C. This is due to the combination of tire constituents NR, BR, SBR, moisture, oil, plasticizer and additives. The pyrolysis takes place through many steps as proposed in the following diagram [22]:



The result was that the important parameters in pyrolysis are: temperature, sample weight and its loss rate, time and heating rate, with very little effect due to the size of the rubber. When heating rate increases, the weight loss is shifted to a higher temperature range and the weight loss rate is increased. The reaction time is shortened but the total weight loss has no obvious change.

Sermin et Al [7] studied the pyrolysis of oily waste from ships [bilge water oil (BW), oil sludge (OS)], scrap tired (ST) and co-pyrolysis of a mixture of them BW:OS:ST

1:1:2 at 400°C and 500°C in absence and presence of catalyst figure 1-8. A commercial fluid catalytic cracking catalyst (FCC) and Red Mud (RM) were used as catalyst. The increase of temperature led to a considerable increase both the degradation rate and of the oil yield. The catalysts tested in this study showed similar catalytic activity on degradation of waste. The pyrolytic oil derived from scrap tire contained considerable amounts of aromatics, while co-pyrolysis of scrap tires with oily waste from ships in absence/presence of FFC catalyst produced oils with high amounts of paraffin and low amounts of aromatics figure 1-9.

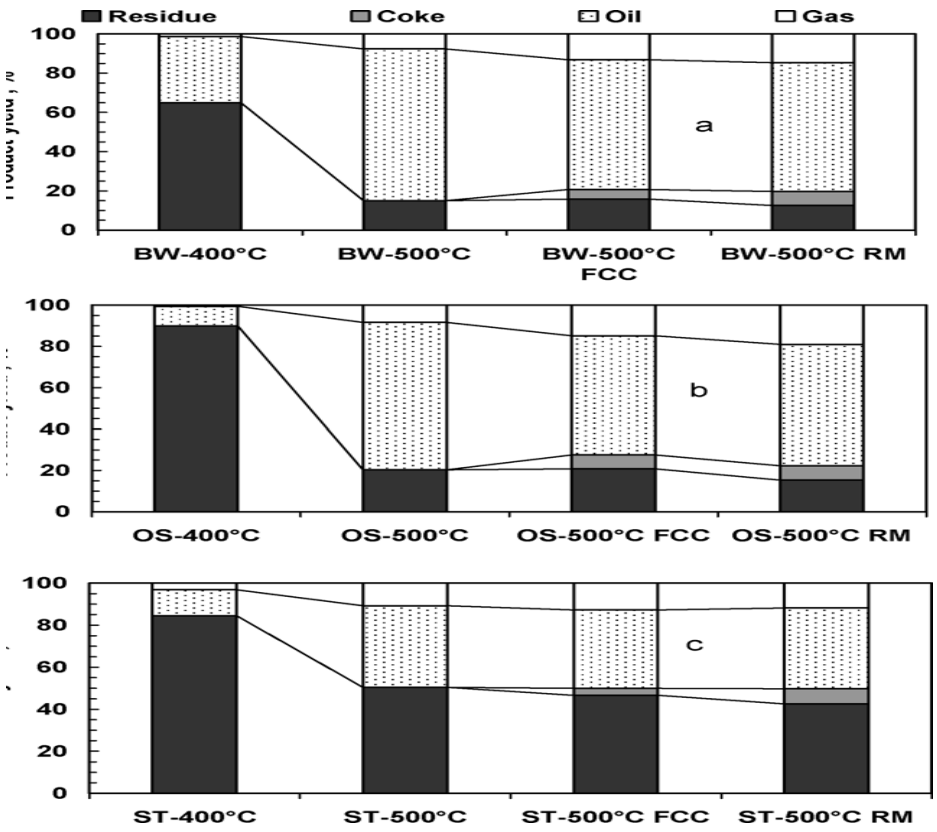


Figure.1- 8. Co-pyrolysis of oily waste with tires[7].

Hydrocarbon content of pyrolsis oils (vol.%).

	Aromatics	Paraffins	Olefins
BW	9.2	83.6	7.2
BW FCC	10.4	76.1	13.5
BW RM	8.5	84.3	7.2
OS	8.1	84.6	7.4
OS FCC	10.3	80.5	9.3
OS RM	8.6	80.7	10.7
ST	13.9	65.6	20.5
ST FCC	18.4	66.3	15.3
ST RM	18.1	51.3	30.6
BW:OS:ST	10.0	75.3	14.7
BW:OS:ST FCC	11.8	74.1	14.2
BW:OS:ST RM	12.0	69.5	18.5

Table 1-7. Result of pyrolysis with/without catalyst [7]

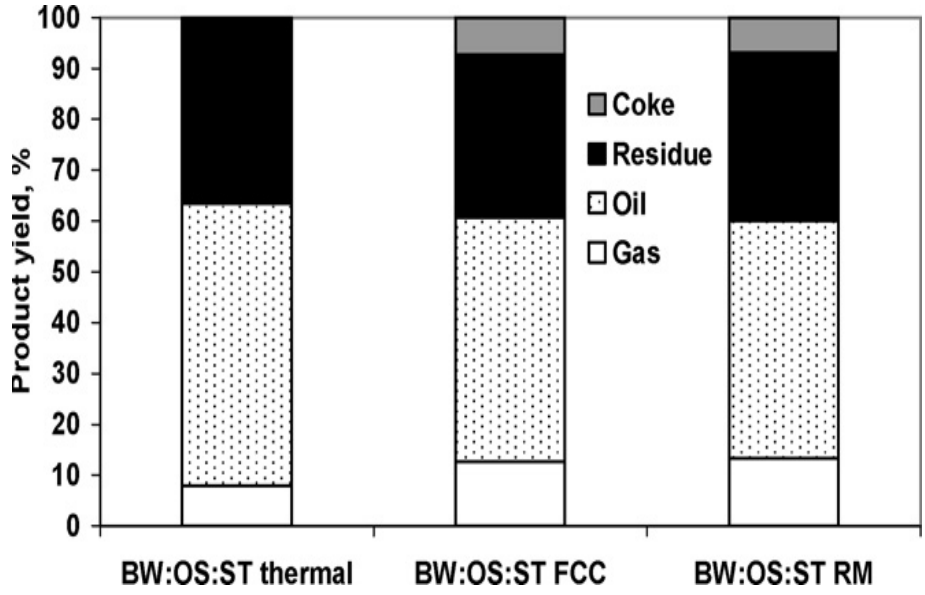


Figure 1-9, Pyrolysis of scrap tires with different waste at different temperature with and without catalyst [7].

Mark et al [2], studied the conversion of used tires into three marketable products: activated carbon, carbon black, and Boudouard carbon. The production of carbon black and Boudouard carbon is a novelty in tires pyrolysis. The pyrolysis process took place at 900°C, with a very flexibility in the process, for example, there was option to reintroduce part of the pyrolytic oil into the reactor to undergo another partial cracking in purpose to increase both solid and gas yields. Solid residue is used to produce the activated carbon using CO_2 stream at 900°C, while the oil product is used to produce black carbon in another furnace at 1400°C to 1700°C by partial combustion. Because the properties of produced oil are similar to those of the petroleum fraction used in carbon black manufacturing. Another product is Boudouard carbon which contains zero-hydrogen, enough small particle size to burn in completely in a diesel engine. Boudouard carbon is produced by reaction of activated carbon with CO_2. Part of the produced gas is used to support the processing needed heat, another part is used in the activation process of carbon and Boudouard carbon, and the rest is often burnt in an outside flare. The resulted work of above mentioned workers has been summarized in the table 1-8:

Reference	Char yield	Oil yield	Gas yield	Conditions and parameters		Remarks
Williams et al [8]	36.7	33	22.2	Pyrolysis	pyrolysis-gasification. Two stage experiment Pyrolysis at 500°C then catalytic gasification at 800°C Ni-Mg-Al	Produce of hydrogen and gases mainly. Ni-Mg-AL was deposited with large amounts of filamentous carbons 31%wt.
	32.8	42.6	26.5	Steam gasification		
	49.5	20.3	43.1	Catalytic steam gasification		
M. Rofiqul et al [1]	40.5	51	8.5	internal heated fixed-bed fire-tubing, 475°C, particle size is 4 cm3, vapor residence time is 5 sec		Production of oil is the object
I. de Marco et al [10]	38-39	20-29	31-41	Heavy ASR	heating rate is 15°C/min, temperatures 500°C, reaction time 30 min, in nitrogen atmosphere	
	58.5-69.4	7.1-8.8	23-33	Light ASR		
Ka-Leung et al [3]	Saved 21.7% of the energy required for pyrolysis process			particle with radius of 3 cm in a batch reactor , heating rate of 10°C/min and target pyrolysis temperature of 510°C in nitrogen atmosphere.		The pyrolysis process consists of two reactions: endothermic reaction and exothermic reactions, they gained 21.7% of energy
Jasmin SHAH et al [4]	The obtained activated carbon was similar to that one available commercially in comparison with surface area 990 m^2g^{-1}/ 800-1100 m^2g^{-1}, elemental analysis and adsorption capacity of methylene blue				450°C ,atmospheric pressure , batch reactor of glass tube ,feedstock of 10 g, heating rate of 20°C and 2 hours	obtain activated black carbon

					reaction time	
E. Aylon at al [5]	39-36	44.5-55	1.8-6.8		conical spouted bed reactor ,15 kg/h of waste tire, 425-600°C range,	Investment conical spouted reactor
Xinghau et al [6]		48		Without catalyst	vacuum (3.5-10 kPa), 550°c	Effect of catalyst on oil yield
		50		3% NaOH powder		
Lopez et al [18]	39.9	46.2	13.8		Distillation -at 550 ºC, atmospheric pressure ,controlled amount of oxygen	
			97.5% Syna-gas (H_2+CO)		Gasification of resulted black carbon,15 atm, in the presence of steam	Gasification of solid residue
Mahmood et al [19]	32.5	51.0			temperature 430°C, inert gas flow rate 0.35 m^3h^{-1} and particle size of 10 mm. in a fixed bed batch reactor	Box-Wilson technique of experimental design, computer program called "optimization technique" have been used to study the optimization of pyrolysis
Adéla et al [20]	39	44	16	Laboratory scale	The difference to 100% is water and ash.	Comparison between laboratory and pilot scale
	39.16	51.47	8.94	Pilot scale		

					Heating rate 2.7°C/min, residence time 60 min, temperature range 175-600	
Fernandez et al [21]	40/38	54/56	8/6	Granulated rubber	Temperature 500°C/900 °C	Comparison of temperature and raw materials
	36/38	52/52	8/12	Textiles fibers		
Jasmin et al [23]	35.8	39.8	24.4	MgO as catalyst	350°C for 2 hours catalytic pyrolysis in a batch reactor under atmospheric pressure	Both catalysts produced 25 wt% of aliphatic hydrocarbons in liquid portion, but with the use of MgO the aromatic increased (55%) and polar hydrocarbon decreased (20%) as compared to catalyst $CaCO_3$ (50% aromatic and 25% polar hydrocarbons).
	35.2	32.2	32.5	$CaCO_3$ as catalyst		

Table 1-8:Summary of some literature works

1-VII Conclusion

It is clear that the pyrolysis conditions related to many different aspects as: objective of pyrolysis (fuel, feedstock…) and composition of tires. For that it is very important to optimize these conditions as precise as possible.

TGA is considered the most useful and unavoidable technique to give initial idea about these conditions, specially, to determine the maximum temperature at which the pyrolysis could be arrived and completed, and the time that is necessary to stay at this temperature.

Then, lab scale optimization is the second intrinsic step in order to determine well the conditions. Lab scale work is the start point toward the pilot scale or industrial plant.

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Chapter 2 Elementary analysis Thermo-gravimetric Study

2-1 Methodology

Tire pyrolysis demands many steps starting from the raw material collection arriving into final pyrolytic products.

Step 1: raw materials identification

Raw material is brought from a collection company of scrap tires in Pays de la Loire region, France. It is heterogeneous pieces of scrap tires with different dimensions varying between 1×1×1 cm^3 and 2×5×9 cm^3 thickness×wide×long respectively, Photo 1. It is not shredded (separated) but it still contains metal and textile. Raw material will be used directly in the reactor for economic reason; as shredding of metal and textile from rubber is time and energy consumed process. In addition, the metals separation process is easiest and demands only simple grinding of solid residue which is very fragile. Then metal will be picked up simply using magnetic bar.

Photo 1, Raw material scrap tires' pieces.

Step 2 : Elementary Analysis

Elementary analysis of raw material gives good idea about the concentration of C, H, S, N, and O. From one hand, C and H concentrations, in addition to the ratio C: H, evaluate the valuation of the pyrolysis process. When the C and H are high and the ratio C: H is small; this means that the raw material is very valuable to be pyrolysed.

From another hand, sulfur (S) presence is undesirable because it diffuses in the three products. This demands completed treatment where ever it is: in the liquid, solid or/and in the gas product. If the conditions of pyrolysis keep the majority of Sulfur in solid or /and gas products; it is better than its transition into liquid product. As Sulfur treatment in the liquid is more difficult than its treatment in the other two products. Indeed, EN590 standard requires very low level of S (10 ppm) in the liquid product when it is used as fuel. The same could be said about the N concentration.

Oxygen presence in the scrap tires increases the oxidation process (mainly combustion in addition to other complicated ones), producing more CO_2 and CO at the expenses of other gases. Combustion process reduces the viability of the pyrolysis.

So, high concentration of C and H, small ratio C: H and low concentration of S, N and O give higher energetic valorization to the scrap tires pyrolysis.

Scrap tires differ from each other in their chemical composition; either at the phase of their manufacturing or because of the way and conditions of using till their being scraps. So, it is necessary to do elementary analysis in order to determine their chemical composition before starting pyrolysis in order to evaluate them energetically.

Elementary analysis has been done using FLASH EA 1112 series CHNS-O analyser with limit of detection 0.2% for each element and sample weight range is [0.5-1] mg.

Step 3: Thermo-Gravimetric Analysis (TGA)

After the elementary analysis step, and the decision that the raw material is evaluated to be pyrolysed, TGA is the intrinsic step to determine the approximated conditions of pyrolysis.

TGA helps to determine the range of temperature where the pyrolysis takes place, the temperature at which it is necessary to heat up the raw material (T_{max}); the time that the scrap should be stay at T_{max}, the effect of heating rate, the effect of inert gas flow rate, and finally the yield of volatile products (gas and liquid). Volatile yield is the most important information that could be obtained from TGA in addition to T_{max}.

TGA helps, as well, to calculate the kinetic parameter of degradation process; activation energy E_a, potential factor A, constant factor and order of degradation (pyrolysis) reaction. These kinetic parameters and its importance will be discussed in more details in the next chapter (TGA study).

Thermogravimetric instrument brand is SETARAM Setsys Evolution 16/18 TGA-DSC. Sample weight range [50-200] mg, max temperature is 1700°C and inert gas (nitrogen) flow range is [4-200] ml/min.

Step 4: lab-scale pyrolysis optimization

In the previous step – step3 1-VI.3- , information about the pyrolysis conditions could be obtained. But, the values of these conditions are not precise because of many work aspects:

i. In the TGA analysis, the raw material is grinding in very fine powder (Ø≈ 250 μ).
ii. Because of finesse of raw material, particle is considered as spherical shape, then, the resistance of heat transfer is homogeneous and very weak.
iii. TGA used very small amount; 50 ~ 150 mg; this quantity does not reflects the sample entirely.

For that, optimization of condition on the lab or pilot scale is necessary to have an idea more precise about the pyrolysis conditions.

A 19 cm diameter and 24 cm height cylindrical, stainless steel, fixed-bed, external electrical wall heated batch reactor was used. Its total capacity of WT is ≈ 1500 g. The reactor was purged using a 100 mL/min nitrogen flow for 30 min at the beginning of each experiment. To make sure that the system is full with inert gas and no oxidation process will take place, gas analysis is done at the end of purging. The produced vapour pushes itself out into a water-cooled (15°C) condenser, where liquid fraction is condensed in the receiving flask. Samples of non-condensing gases are taken each 10-15 minutes to be analyzed in a micro GC instrument in order to identify the gas composition.

Two thermocouples are attached to the reactor, the first is located at the middle of the reactor (central point), while the second is located on the outlet of reactor before the condenser. The first thermocouple measures the temperature inside the reactor while the second measures the temperature of produced vapour.

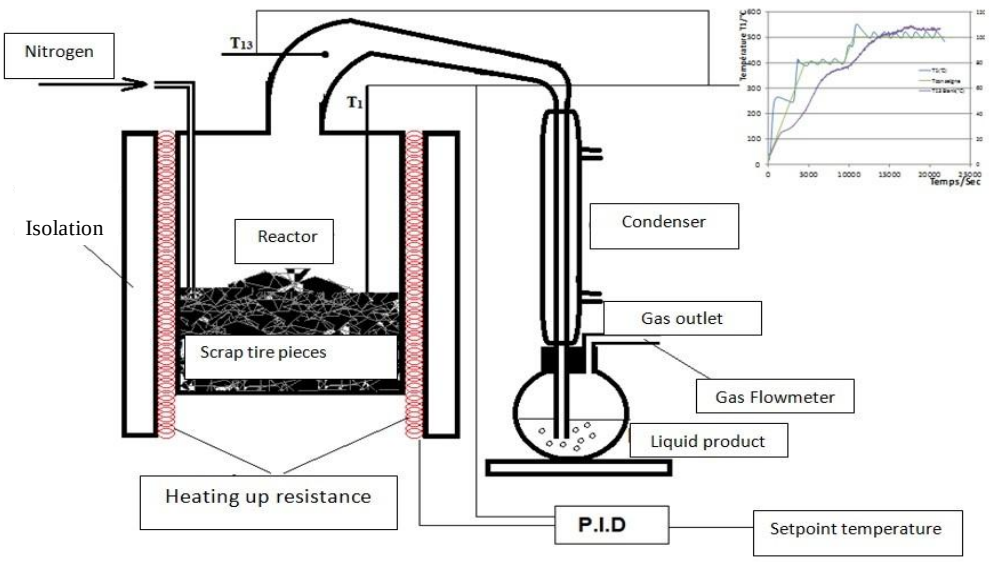
The collected liquid in the receiving flask is filtered from carbon, solid particles and heavy gum compounds (<1%). Then the liquid is characterized (density, viscosity, flash point, GCV and GCMS). Simple schema about the purolysis system is shown in schema 1.

Step5: product physico- chemical characterization and evaluation

To evaluate the ability of product use as fuel or feedstock, physico-chemical characterization should be done. These characterizations are mentioned in the European standard EN590. In addition to the characterization of EN590, engine performance should be evaluated.

Description of analytical instruments, used in product characterization, is as follow:

Flash point was measured using NORMALAB NPM 440 instrument; it measures up to 350°C. Viscosity was done using AND vibro viscometer SV-10, with measuring range 0.3-10 000 mPa.s. GC-MS has been achieved using PerkinElmer Gas chromatography; Clarus 680, with mass spectrum detector of PerkinElmer; Clarus 600S. GC is supported with Capillary column: 30m×0.25mm×0.25µm film thickness; fused silica; ALB^{TM}-5ms; Suplco. In addition; Gross Calorific Value (GCV) has been obtained using Parr 6200 calorimeter; upper limit of detection 8000 cal/g and upper limit of weight is 1g. Finally, gaseous products were analyzed using Micro-GC: Agilent technologies 3000A; it determines H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, CO, CO_2, O_2 and N_2. The pyrolysis steps is summarized in the following chart, chart 1



Schema 1. Pyrolysis system.

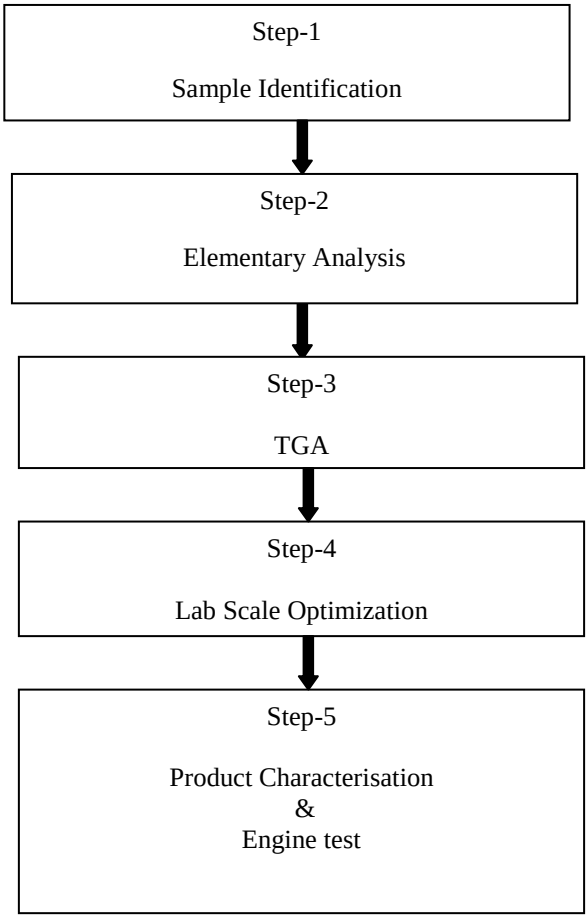


Chart 1, pyrolysis steps

2-II Elementary analysis

2-II.1 Introduction

Elementary analysis gives information about the concentration of C, H, N, S and O elements. The concentration of both C and H, in addition to the ratio C:H, are the key factors to decide if the raw material is suitable to be pyrolysed.

2-II.2 Result and discussion

Average and standard deviation of 10 runs of elementary analysis is showed in table 2-1:

Element	**N** (%)	**C** (%)	**H** (%)	**S** (%)	**O** (%)
Average	0.04	84.21	6.90	2.73	6.31
Standard Deviation	0.007	2.07	1.13	0.61	1.84

Table 2-1, Elementary analysis of used scrap tires.

Comparing with result of references [13 - 25]. N concentration is lower than these mentioned in the references which ranges between 0.17 and 2.3. While, there is high agreement for the concentration of both C and H which are range between (75.4 – 86.7), (6.54 -8.10) respectively. Sulfur content is upper (1 -2).

2-II.3 Conclusion

Then, elementary analysis encourages the pyrolysis of used raw material. But it demands post-pyrolysis treatment of products because of higher sulfur content.

2-III Thermo-Gravimetric Analysis (TGA)

2-III.1 Introduction

Thermo-Gravimetric Analysis / Derived Thermo-Gravimetric (TGA/DTG) study is the very indispensable starting step of the pyrolysis process in order to choice the optimal operating conditions (Heating rate, Flow Rate and maximum temperature T_{max}), to know the component of the raw material and its kinetic behavior - thermal decomposition process, Arrhenius equation- (pre-exponential factor A, activation energy E_a, constant rate reaction k and order of reaction n). In addition, the yield of volatiles (liquid and gas) and solid products, and the thermal range of degradation [1,5].

As Quek et al [5], and references there in, show in their study for different brands of scrap tyres. The thermal degradation behavior, as well as the kinetic parameters, varies with the change of scrap tyres resource depending on the manufacturing company (formulation specific to each brand) and their own chemical composition. So the TGA/DTG study is very important to be achieved before starting any lab-scale or industrial pyrolysis process. It is not accurate and not recommended depending upon the literature information of others' works.

A series of experiments with three different values of nitrogen flow rate (FR), which are 5mL/min, 50 mL/min and 95 mL/min, has been done in heating range [25°C - 600°C]. This series of experiments has been repeated at three different values of Heating Rate (HR), which are 1°C/min, 5 °C/min and 9 °C/min. In other words, an assembly of experiments at different levels of both FR and HR has been done in order to well study the effects of both HR and FR, then, in the next steps, the component of raw material and the degradation kinetic behavior have been investigated.

2-III.2 Influence of inert gas Flow Rate (FR)

Three values of FR have been applied which are: 5mL/min, 50mL/min and 95mL/min. These experiments have been repeated with three different values of HR which are: 1°C/min, 5°C/min and 9°C/min. Each experiment has been repeated two

times at least. Sample weight is about 100 mg. The results of TG and DTG curves are in the following curves (figures 2-1, 2-2, 2-3, 2-4, 2-5, 2-6) and table 2-2:

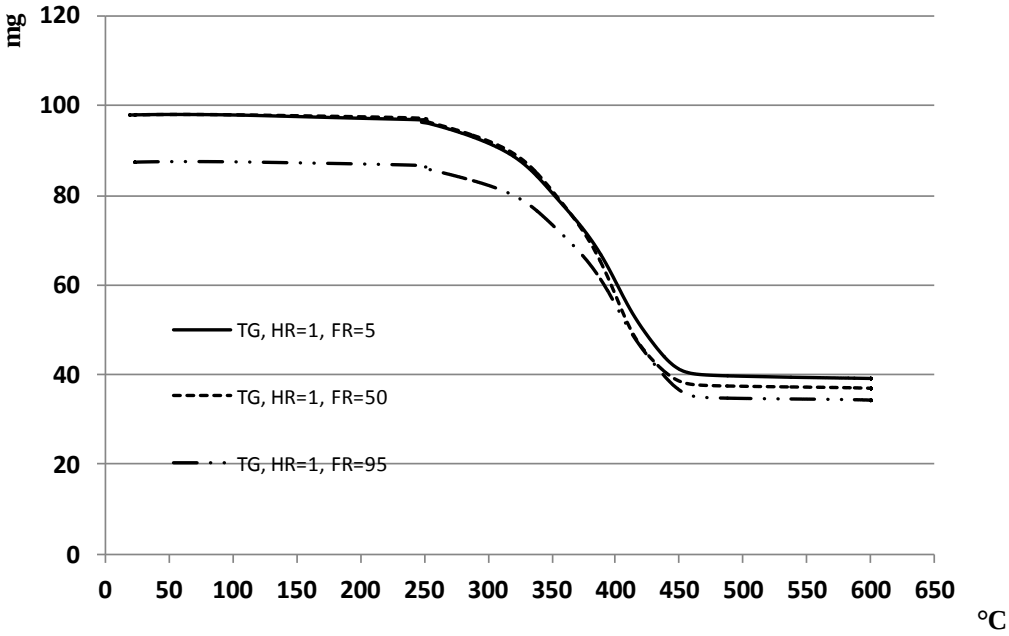


Figure 2-1, TG of three different FR at HR 1°C/min

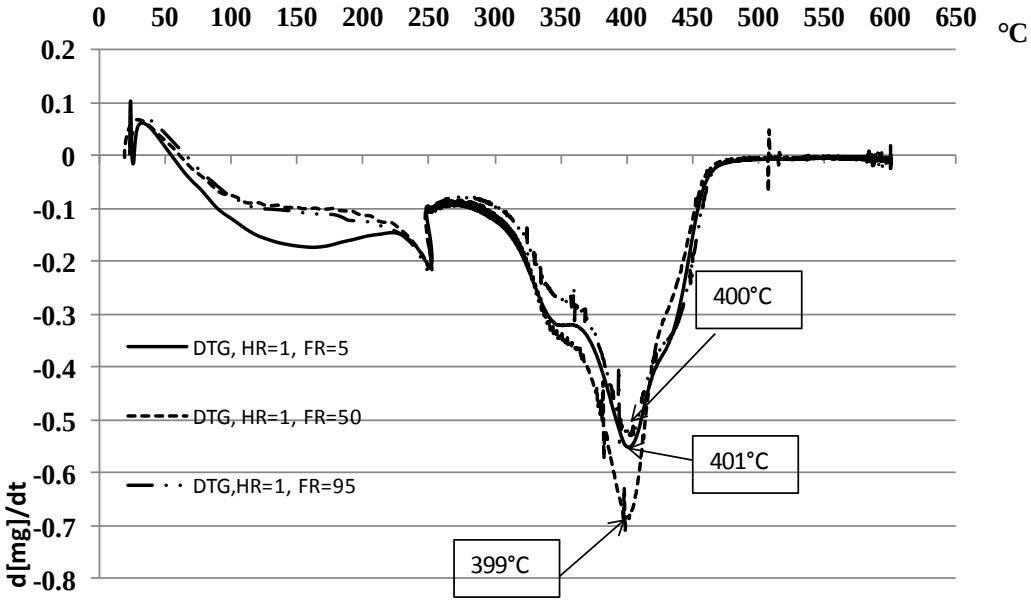


Figure 2-2, DTG of three different FR at HR 1°C/min

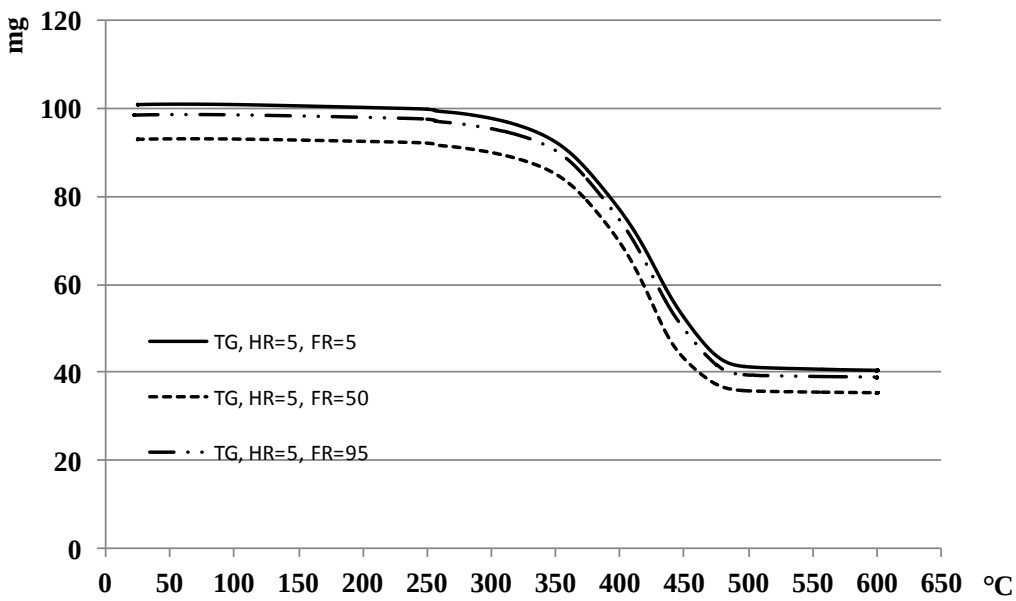


Figure 2-3, TG of three different FR at HR 5°C/min

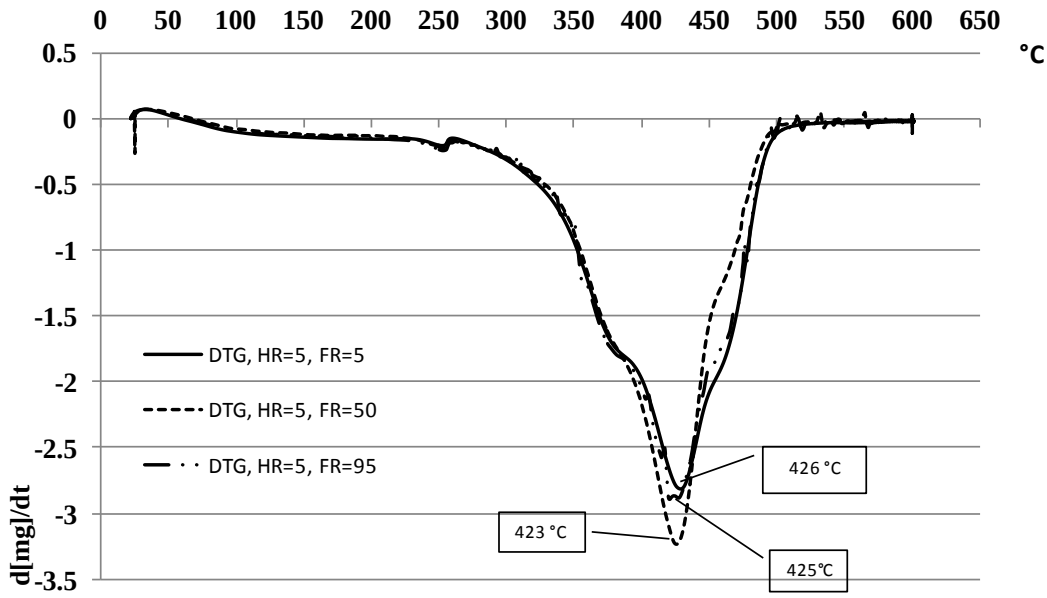


Figure 2-4, DTG of three different FR at HR 5°C/min

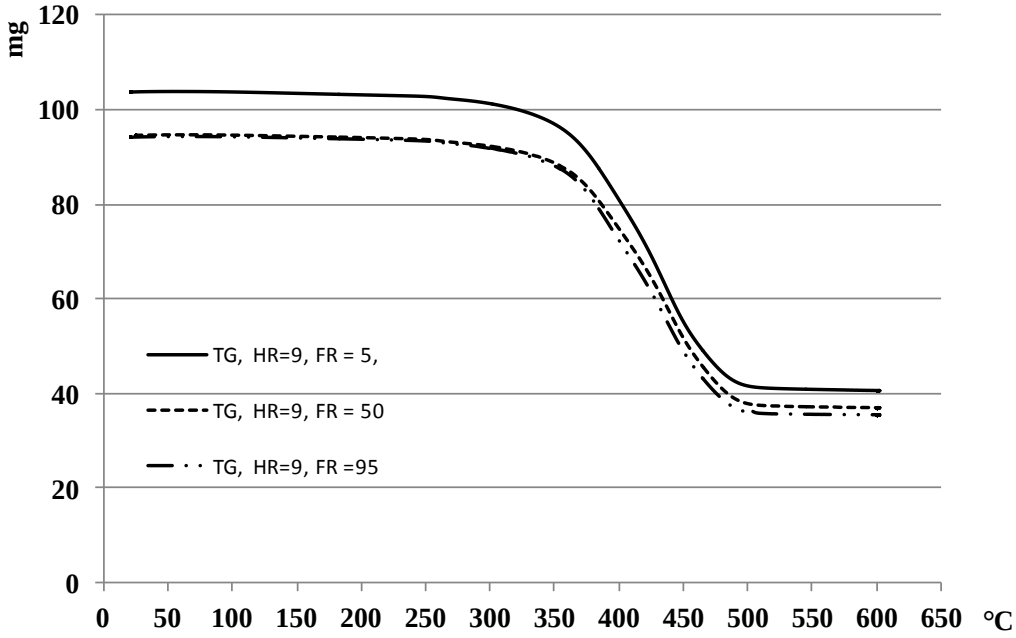


Figure 2-5, TG of three different FR at HR 9°C/min.

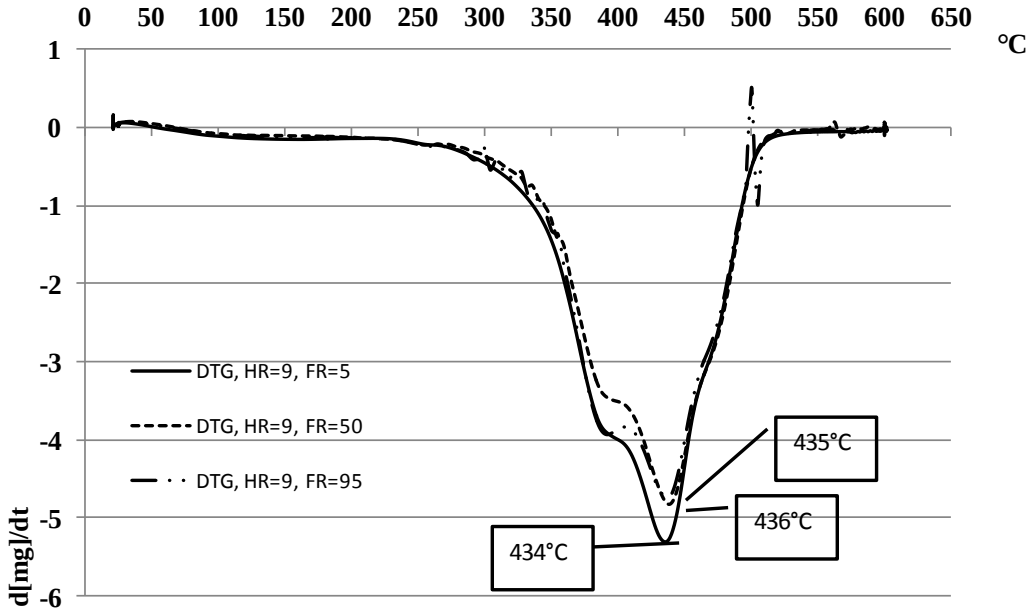


Figure 2-6, DTG of three different FR at HR 9°C/min

2-III.2.1 Results and Discussion

1. Figures 2-1, 2-3 and 2-5, and table 2-2 show that in all levels of both FR and HR values, the pyrolysis takes place in the thermal range from ≈ 200°C to ≈500°C.

2. Figures 2-2, 2-4, and 2-6, and table 2-2 show that for a fixed HR value, the T_{max} and the maximum degradation rate doesn't change dramatically. But they change according to the HR value (it will be discussed in HR influence paragraph)

3. FR doesn't affect the yield of volatile materials, which is around 60%.

Experiment	**Heating Rate** (°C/min)	**Flow Rate** (mL/min)	**sample weight** (mg)	**Yield of Volatile** (%)	**Rang of Degradation** (°C)	**Temperature (T_{max})** (°C)	**Maximum degradation rate** d[mg]/dt (mg/min)
1	1	5	98.2	58.21	170- 480	≈ 400	0.55
2		50	97.9	61.63	100 - 467	≈ 400	0.70
3		95	88	60	160 - 471	≈ 400	0.55
Average				59.95			0.60
Standard Deviation				1.71			0.09
4	**5**	**5**	101.1	58.65	180 -504	≈ 425	2.81
5		**50**	93.2	60.9	150 - 504	≈ 425	3.23
6		**95**	98.6	59.8	180 - 500	≈ 425	2.88
Average				59.78			2.97
Standard Deviation				1.13			0.23
7	9	5	103.8	61.84	150 -515	≈ 435	5.30
8		50	94.8	60.15	100 - 522	≈ 435	4.82
9		95	94.1	62.1	110 - 512	≈ 435	4.75
Average				61.36			4.96
Standard Deviation				1.06			0.30

Table 2-2, Results of TG and DTG

Degradation range [200°C - 500°C], volatiles' yields and T_{max} values, which are in good agreement with some researcher's work [1, 3, 5], show that no significant effect is carried out by inert gas FR. Actually, there are two main reasons for this phenomena at the TGA scale.

The first reason is the method of inert gas (nitrogen) insertion, as the principal role of nitrogen is to provide inert atmosphere inside the reactor and to get rid of oxygen avoiding combustion process. Theoretically, nitrogen can play additional paramount role which is helping to carry out the produced vapor outside the reactor (crucible in the case of TGA); and accelerating the evaporation process. In other words, it speeds up the pyrolysis process and decreases both the consumed energy and the T_{max}. In addition, some researchers [2] found that carrier gas removes the volatile products from the external reaction zone, and hence reduces secondary reactions (cracking and char formation) to a lowest pronounced extent [1, 6]. Actually, nitrogen introduction inside the used TGA instrument is as shown in figure 2-13. This means that nitrogen doesn't enter inside the crucible, like in the lab-scale or industrial pyrolysis reactor. Instead of carrying out the produced vapor outside the crucible, it; maybe; enforces them to stay more time exposing into more side reactions.

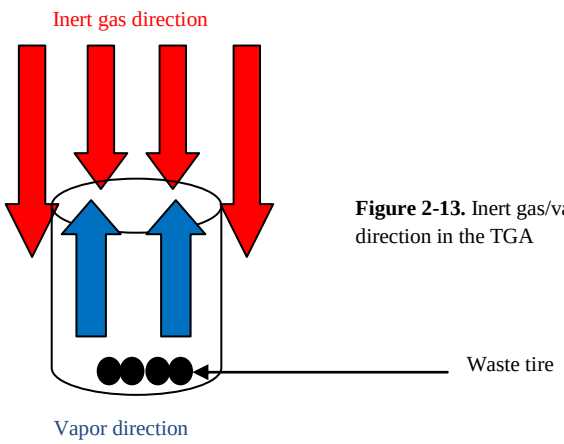


Figure 2-13. Inert gas/vapor direction in the TGA

The second reason is, depending on B. Lah et al [1] and William et al [30], the sample weight is so small *(≈ 100 mg)*, and the form of analyzed sample is as fine as powder /φ < 1mm / (*to be able to measure this little quantity)*. This makes both the temperature and the material distribution in the crucible relatively homogenous. This is different from the lab-scale case.

2-III.2.2 Conclusion

FR has no significant effect on the pyrolysis process at the TGA scale. These findings are in agreement with some different researchers' [1, 6]. FR effect should

be well studied again at lab scale (where: sample weight ≈ 500- 1000 g; nitrogen enters inside the reactor).

2-III.3 Influence of Heating Rate (HR)

Three values of HR have been applied which are: 1°C/min, 5 °C/min and 9°C/min. These experiments have been repeated with three different values of FR which are: 5mL/min, 50mL/min and 95mL/min. sample weight is about 100 mg. At least, duplicate of each experimental run have been done. The results of TG and DTG are in the following curves (figures 2-7 to 2-12) and table 2-3:

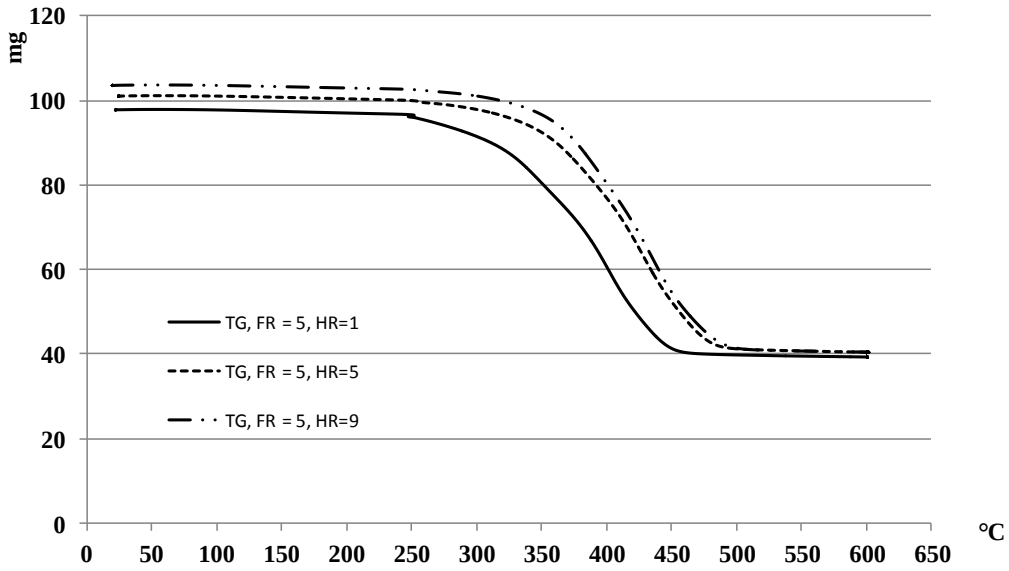


Figure 2-7, TG of three different HR at FR 5 mL/min.

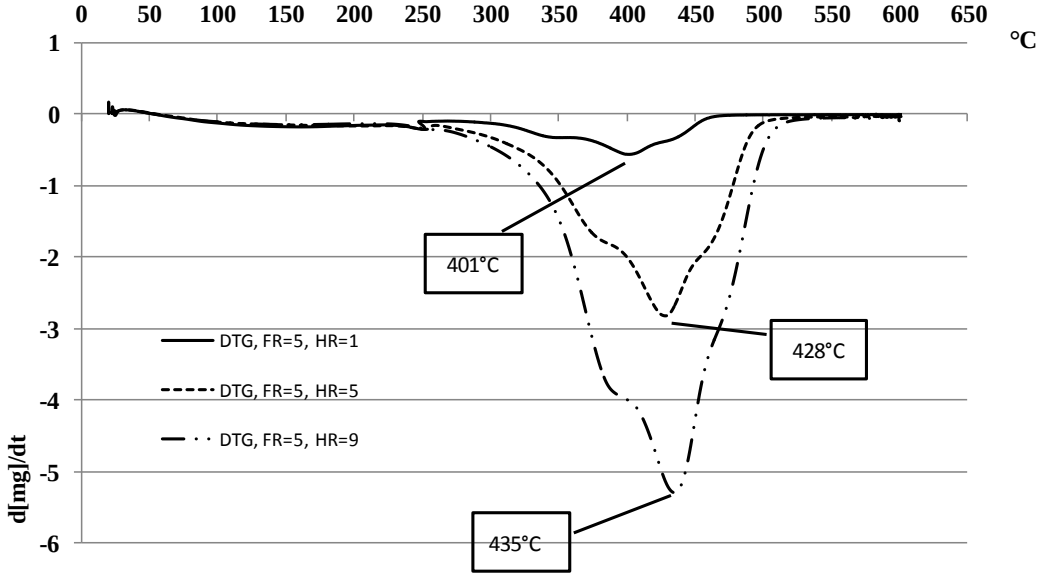


Figure 2-8, DTG of three different HR at FR. 5 mL/min

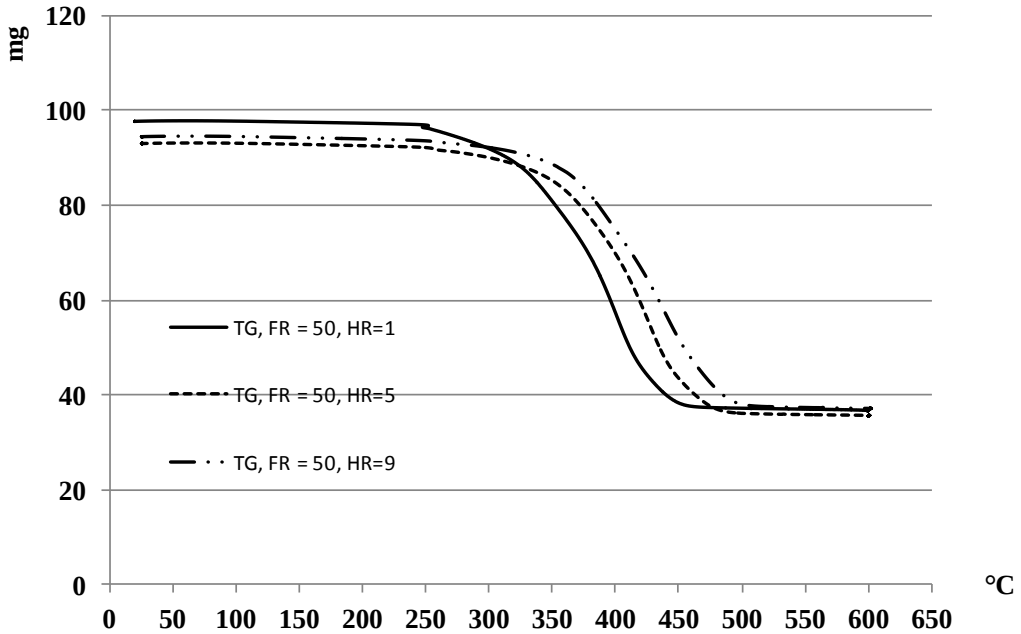


Figure 2-9, TG of three different HR at FR 50 mL/min.

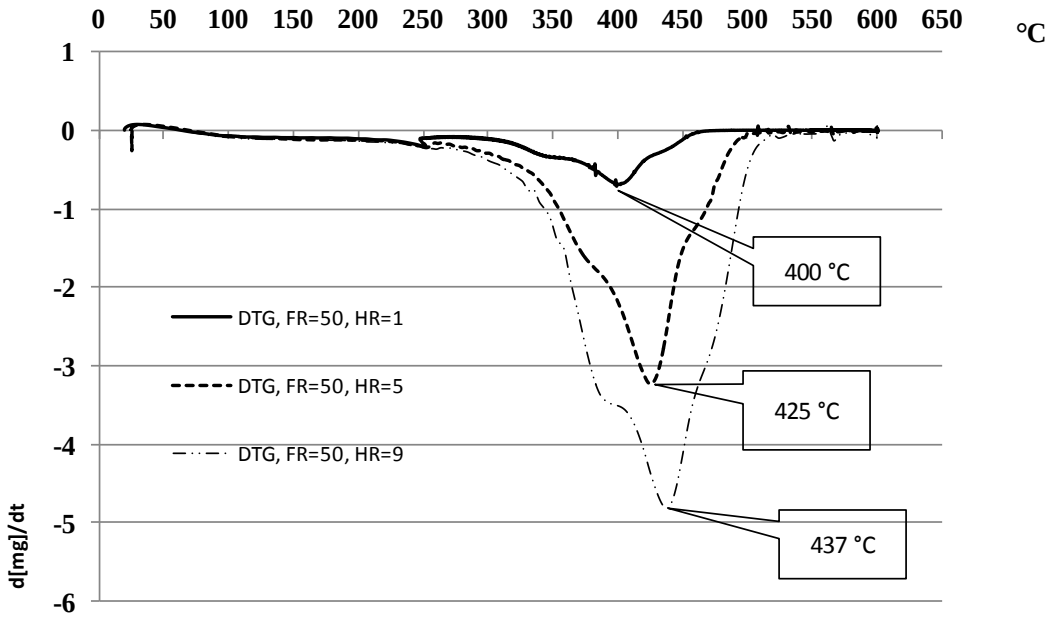


Figure 2-10, DTG of three different HR at FR 50 mL/min.

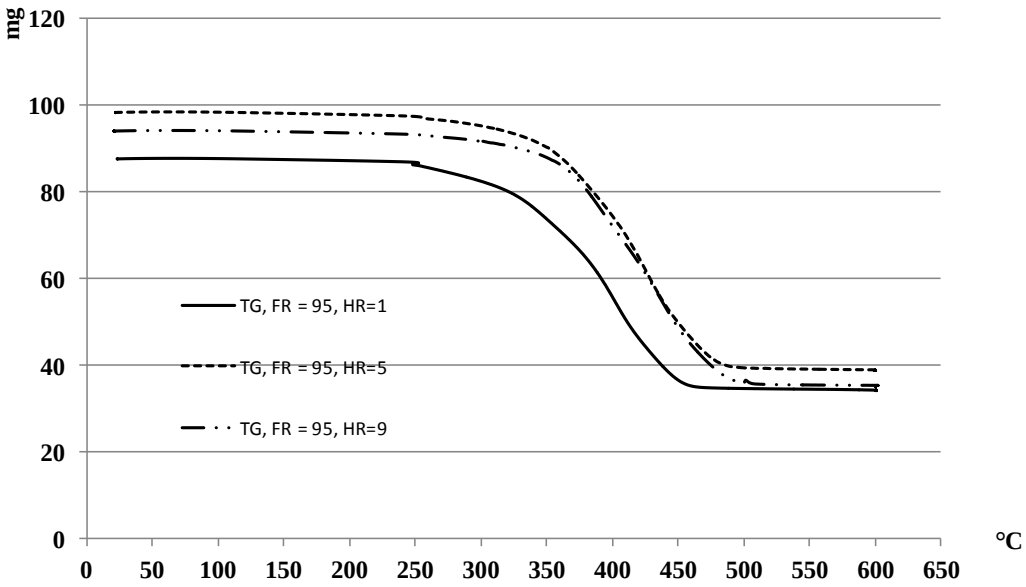


Figure 2-11, TG of three different HR at FR 95 mL/min.

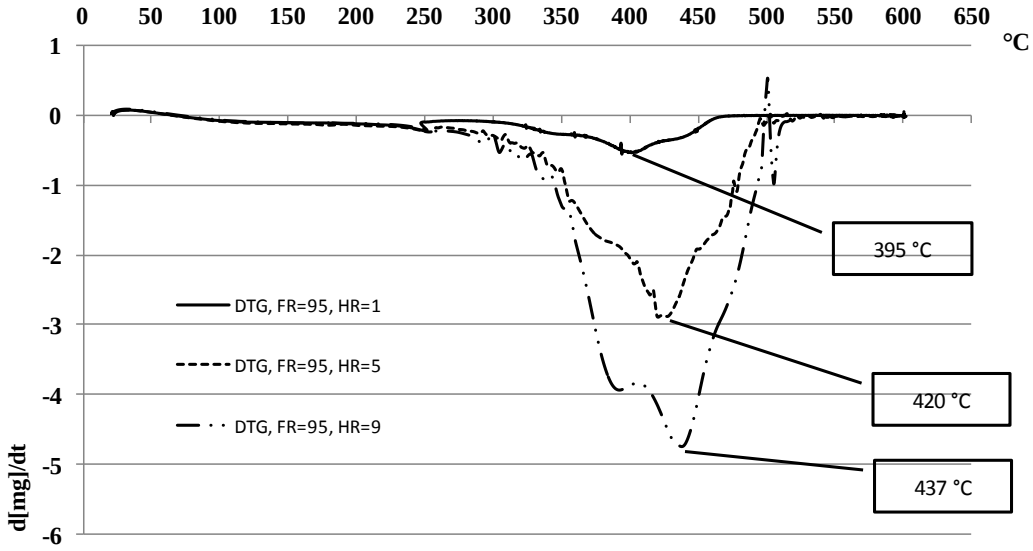


Figure 2-12, DTG of three different HR at FR 95 mL/min.

2-III.3.1 Results and discussion

1. Figures 2-7, 2-9 and 2-11, and table 2-3, show that in all levels of HR and FR, the thermal range of degradation is from ≈ 200°C to 500°C. And the yield of volatile products is always around 60%.
2. T_{max} increases considerably with HR increment. Maximum degradation rate as well.
3. Figures 2-8, 2-10, and 2-12, in addition to the previous figures 2-2, 2-4 , and 2-6, show four distinguished degradation zones which are the following (depending on HR value; fig 2-4 as example) :
   I. Zone I: wide degradation zone, from 200°C into 300°C.
   II. Zone II: maximum rate of degradation is at around 380°C.
   III. Zone III: maximum rate of degradation is at around 425°C.
   IV. Zone IV: maximum rate of degradation is at 465°C.

Experiment	Flow Rate (mL/min)	Heating Rate (°C/min)	sample weight (mg)	Yield of Volatile (%)	Rang of Degradation (°C)	Temperature (T_{max}) (°C)	maximum degradation rate d[mg]/dt (mg/min)
1	**5**	**1**	98.2	58.21	200 - 500	≈ 400	0.55
2		**5**	101.1	58.65	200 - 500	≈ 428	2.81
3		**9**	103.8	61.84	200 - 500	≈ 435	5.31
Average				59.57			2.89
Standard Deviation				1.98			2.38
4	**50**	**1**	97.9	61.63	200 - 500	≈ 399	0.7
5		**5**	93.2	60.90	200 - 500	≈ 425	3.23
6		**9**	94.8	60.15	200 - 500	≈ 438	4.82
Average				60.89			2.97
Standard Deviation				0.74			0.23
7	**95**	**1**	88.0	60.00	200 - 500	395	0.53
8		**5**	98.6	59.80	200 - 500	420	2.89
9		**9**	94.1	62.10	200 - 500	437	4.75
Average				60.63			2.72
Standard Deviation				1.27			2.11

Table 2-3, Results of TG and DTG

The results, degradation range [200°C – 500 °C] and volatiles' yields around 60% agree with many literatures results.

Tyre consists meanly of:

- Decomposable materials which are: rubber (NR, SBR, and BR) and plasticizer. This part forms about 60% m/m of tyre.
- And non-decomposable elements which are: carbon black, Zinc oxide and steel. In addition to other minor additives.

Degradation (pyrolysis) takes place meanly over the rubber. As the rubber content ranges between 55% and 65% [1, 2, 3, 29 and the ref therein] depending upon the manufacturer. Yield of 60% is considered as a normal consequence.

When the HR increases, the time of degradation (pyrolysis) is reduced, meanwhile, the supplied quantity of heat (energy) by unit of time increases, as a

consequence, the quantity of degraded tyre, by unit of time, increases as well; this increases the rate of degradation. On other hand, when the HR is high, the heat rising up maybe more rapid than the rate of degradation which reflects in shifting up T_{max}. In addition, the rapid rise of temperature increases the evaporation process preventing many side cracking to take place in the vapor phase which is reflected in high rate of degradation (speed mass loss by time). This could affect the physico-chemical properties of liquid products.

The majority of researchers observed the different distinguished thermal degradation zones in TG/DTG curves. And they attributed them to the thermal degradation of different components of tire. Zone I related into mixture degradation of oil, moisture, plasticizer and additives. While the other zones related to different types of rubbers (NR, SBR, and BR) [1, 5, 6, 7, 8, 9]. On the contrary, Korenova et al [2] found only two zones; the first corresponded to volatile and the second one to rubber.

Some researchers found that with increase of HR, the range of degradation increases as well [10-50 °C/min]. This isn't shown here, could be because of that the range of HR [1-9 °C/min] isn't enough to show this phenomenon.

2-III.3.2 Conclusion

HR affects dramatically the tire pyrolysis either by the degradation rate or by the T_{max}. This effect could affects as well the physico-chemical properties of the pyrolytic products? HR; or in indirect words the quantity of supplied heat by time unit (energy) should be well studied on lab-scale work.

2-III.4 Composition of tires (rubber components)

B. Lah et al [1] found that DTG curve consists of three distinguished regions, the first represents the volatile compounds like moisture, plasticizer and additives, while different rubbers, namely NR, SBR and BR in the second and third regions; this accords with many other researchers [5, 6, 7]. In contrary, Korenova et al [2]

has reported that only two regions were observed in the DTG curves, whereas the first one corresponded to volatiles and the second one to rubbers.

As it is known, rubbers (NR, SBR, and BR) form the major part of degradable (volatile) content of tire. Then, for well understand and know the qualitative and/or quantitative composition of used scrap tire, the degradation of these rubbers should be studied individually and in mixture with each other. Then they should be compared with those of used scrap tire under the same conditions.

The conditions that the study has been done at are: HR=5 °C/min and FR=5 ml/min and thermal range of pyrolysis = [ambient °C – 600°C]. NR is available in two forms **Cis** and **Trans**. So, the both forms have been studied in order to make sure that there is no difference in their thermal degradation behavior.

2-II.4.1 Qualitative composition determination

DTG of all individual rubbers and used tires are shown in figures 2-14, 2-15, 2-16, 2-17, 2-18 and table 2-4. As has been mentioned above that there are many degradation zones in tires DTG curves , and as it is asserted in figure 2-14, used scrap tires pyrolysis takes place at three main distinguished zones with T_{max} are around 380°C, 430°C, and 460°C consequently. This doesn't agree with the results of other researchers' works that there are one or two peaks of degradation for rubber components of tire. In addition, there is small peak available at $T_{max} \approx 250$ °C. This peak corresponds to the additives in tires because; in addition to that the pertinence of this peak to the additives in tires is mentioned in many literature works [1 - 5]; it doesn't appear in the standard individual rubbers curves.

Comparing figures 2-15 and 2-16 shows that there isn't difference in the degradation behavior of both forms of NR /Cis and Trans/. While comparing them with figure 2-14 shows that tire degradation around 380°C belongs to NR this accord with B. Lah [1] and William [30]. They showed that NR max rate of degradation is 365°C and 375 respectively. NR degradation starts around 300°C, rate of degradation increases sharply till it arrived at 380°C, then the rate of degradation decreases till 400°C. The degradation stops or becomes very weak in

the thermal range [420°C – 433°C]. Then it resumes till arriving at 490°C, where the degradation is finished. This doesn't accord with William [30] that NR degrades at only one step.

The cease of NR degradation in the range [420°C – 433°C] could be related to the chemical structure crosslinking of NR, which contains different types of chemical bonds. Each chemical bond demands specific amount of energy to be cracked down. In this range [420°C – 433°C], the introduced energy isn't sufficient maybe to crack down any rest available liaison.

Comparing, figure 2-14 with figure 2-17 shows that the degradation with maximum degradation rate at ≈ 430°C belongs to SBR. The degradation starts at around 350°C, increases sharply till arriving at around 430°C, then it decreases, sharply as well, till it finishes at around 480°C. while, B. Lah[1] and William [30] obtained SBR degradation at 447°C and 455°C.

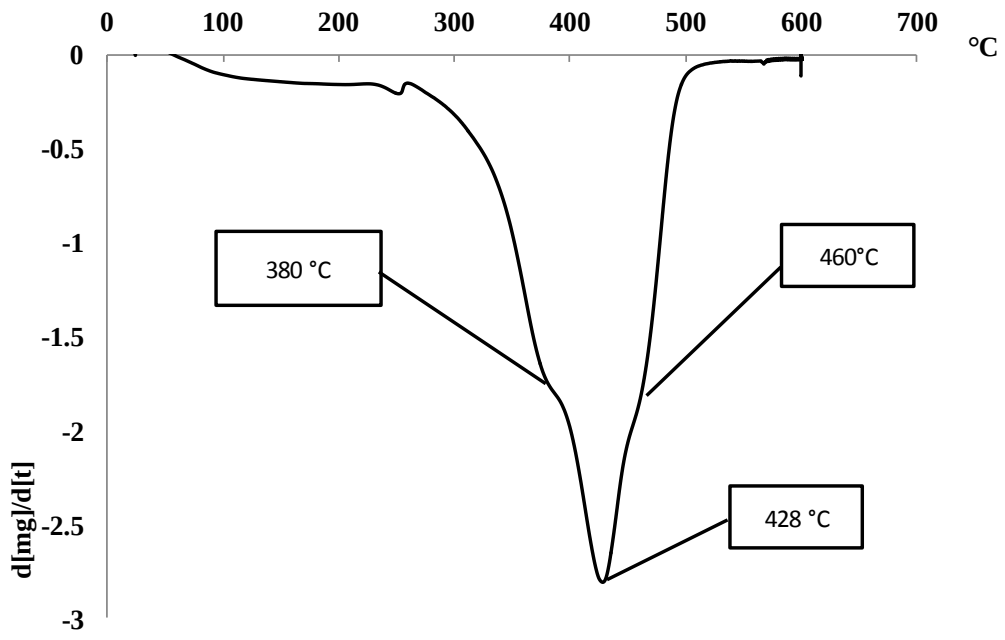


Figure 2-14, DTG of tire. HR = 5, FR = 5.

Figures 2-14 and 2-18 don't make sure that the third main peak in the tire curve, which is around 460°C, belongs to the BR that because its T_{max} is around 475°C in the DTG curve of BR when it is alone. There is shift of 15 °C between the two

peaks in the two figures. While B. Lah [1] showed that BR degrades at 465°C and William [30] showed that BR degrades in two steps at 400°C and 455°C.

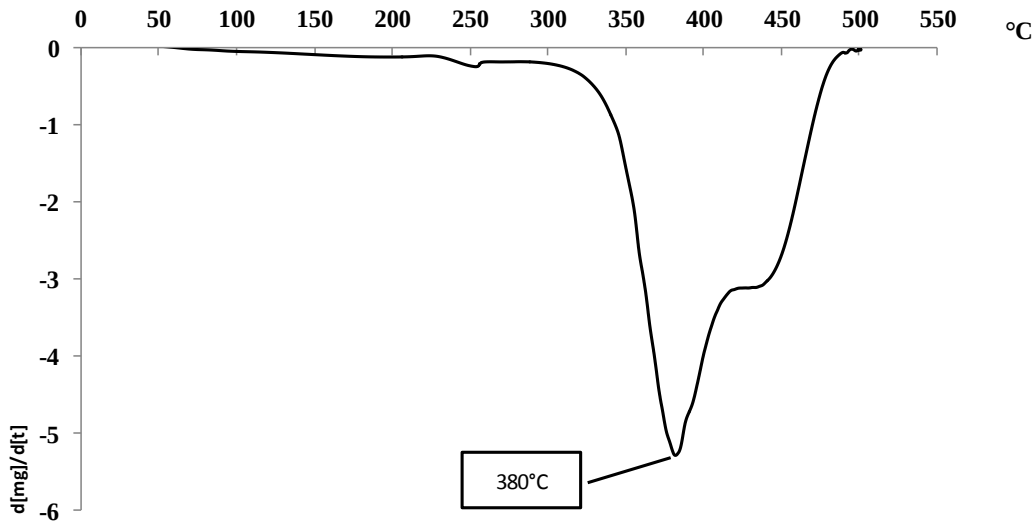


Figure 2-15, DTG of NR-Cis, FR = 5, HR = 5.

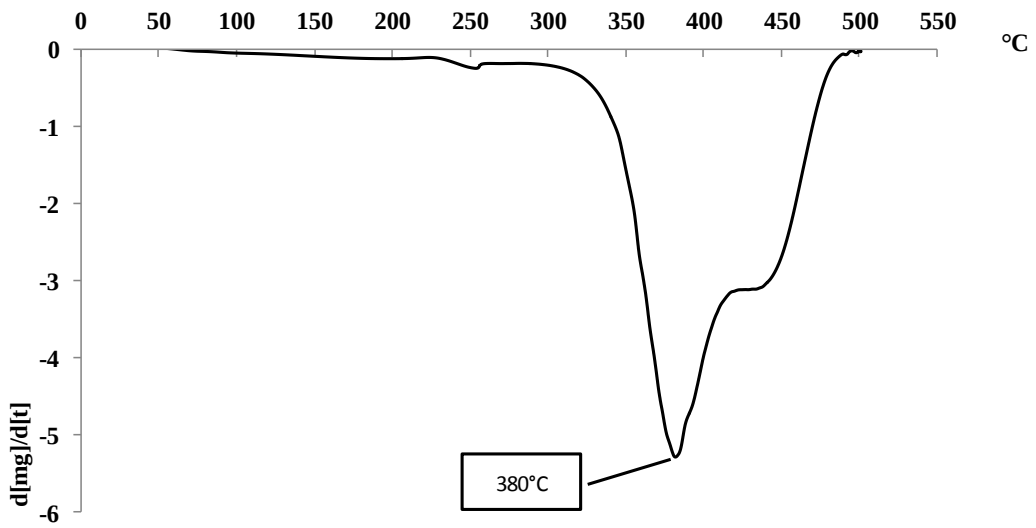


Figure 2-16, DTG of NR-trans. HR = 5, FR = 5

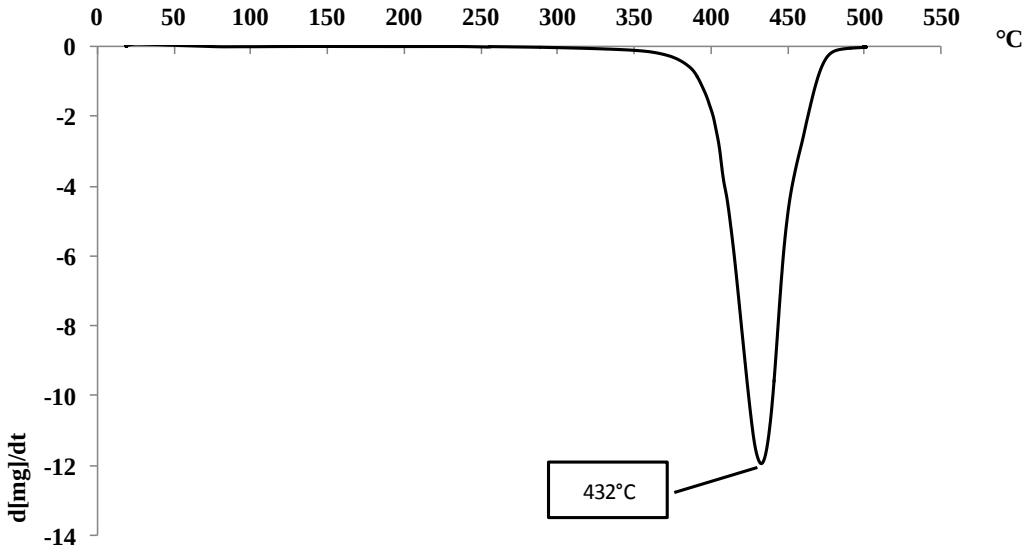


Figure 2-17, DTG of SBR (poly styrene-cobutadiene 4%), HR = 5, FR = 5.

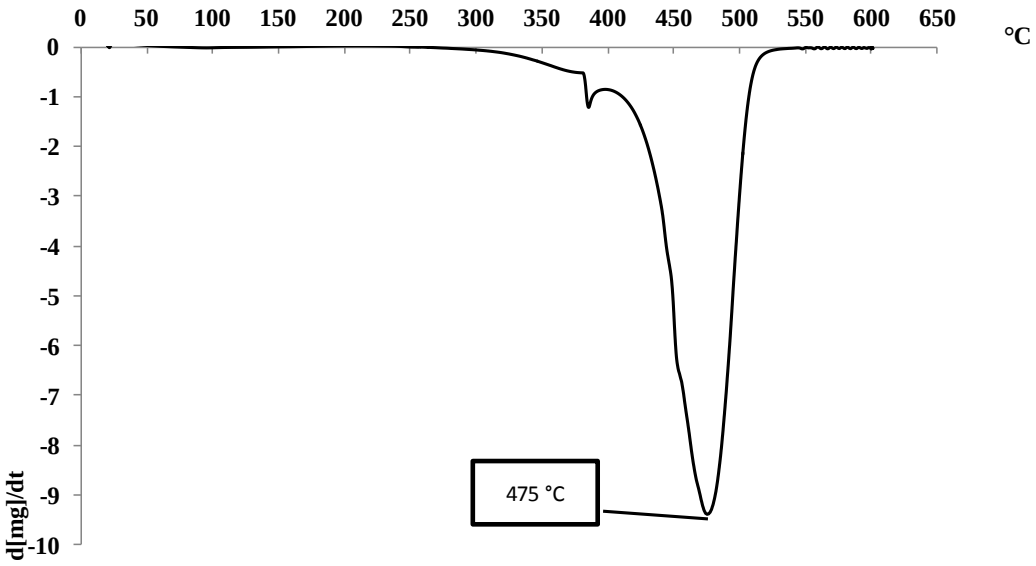


Figure 2-18, DTG of BR. HR = 5, FR = 5.

Rubber	Heating Rate °C/min	Flow Rate mL/min	sample weight (mg)	Yield of Volatile %	Rang of Degradation °C	Temperature max (T_{max}) °C	max d[x]/d[t]
SBR	5	5	93.8	97.32	351 – 480	432	-11.9219
NR-Trans			83.1	98.74	315 – 490	380	-8.5063
NR-Cis			90.4	97.18	315 – 490	380	-5.724
BR			107.2	98	327 – 515	475	-9.3798
Tire			101.1	58.65	180-504	380. 428. 460	-2.8119

Table 2-4, TG/DTG of individual standard rubber and scrap tire.

The question that could be raised up is: Does this peak (at 460°C in tire DTG curve) belong to the BR? To get good answer to this question a series of mixtures (different compositions) of rubbers has been prepared and passed on TGA instrument. The compositions of these mixtures (percentage of rubber) were prepared depending on the following conceptions:

- The concentration of each NR and BR doesn't exceed 40% in the tire[26, 27],
- Normally, NR rubber and SBR are the dominant rubbers in tires,
- Sometimes, BR is added into the tire, and other times it isn't added depending on the manufacturer.

DTG and properties of the mixtures are showed in figures 2-19, 2-20 and 2-21 in addition to table 2-5.

All figures (2-19, 2-20, and 2-21) show that; in standard rubbers mixture; T_{max} of BR is downward shifted to 460°C. This makes sure that in figure 2-14, the third main peak at around 460°C belongs to BR. So, the used tire contains the three main rubbers.

BR's peak is hardly observed in Figure 2-19, it becomes clearer in figure 2-20 and dominant in figure 2-21. The increase in peak clarity in DTG curves accords with BR's concentration increment in the mixtures. The same could be noticed for other rubbers. This can explain the contrary in the literature survey about the number of degradation zones, which related directly to the rubber content in the tire.

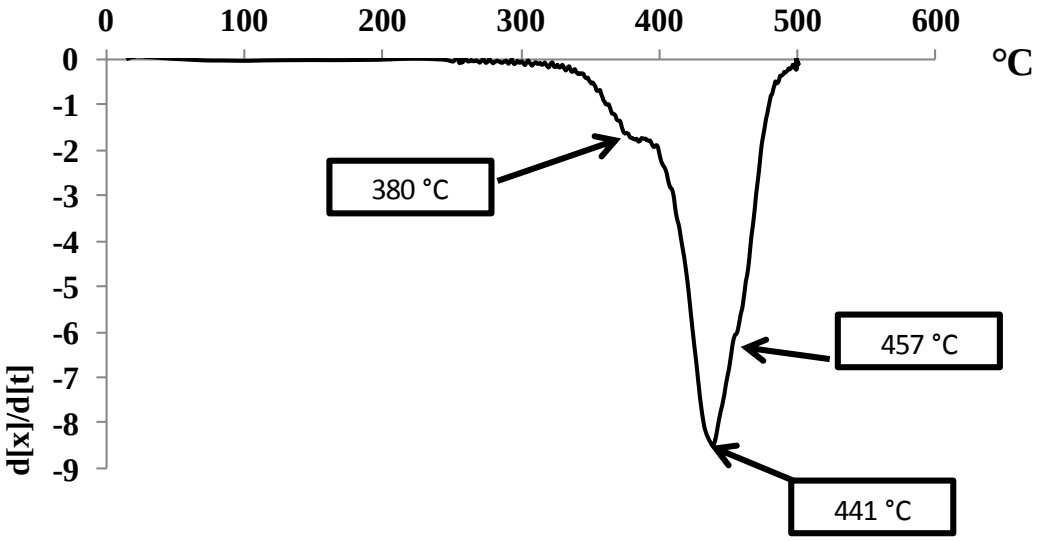


Figure 2-19, DTG of standard Rubber Mixture 1.

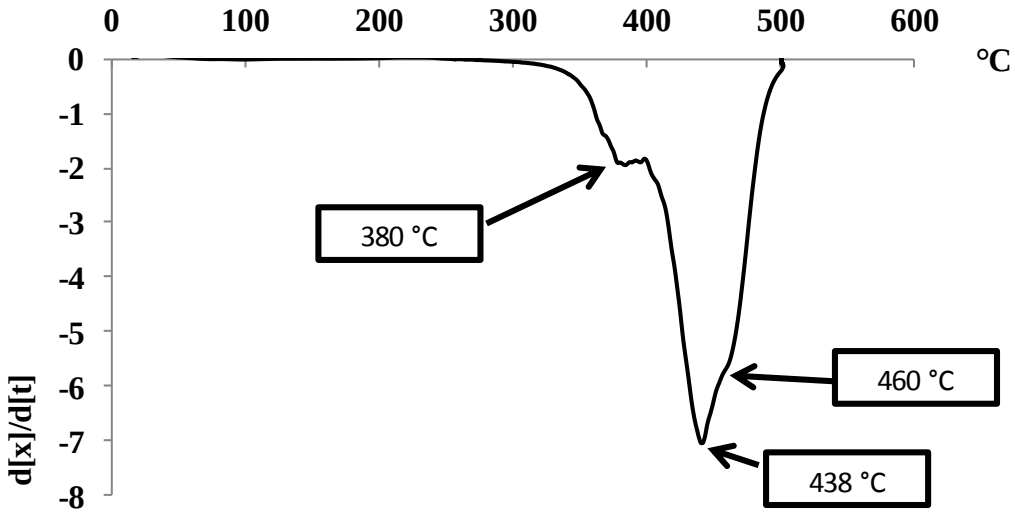


Figure 2-20, DTG of standard Rubber mixture 2

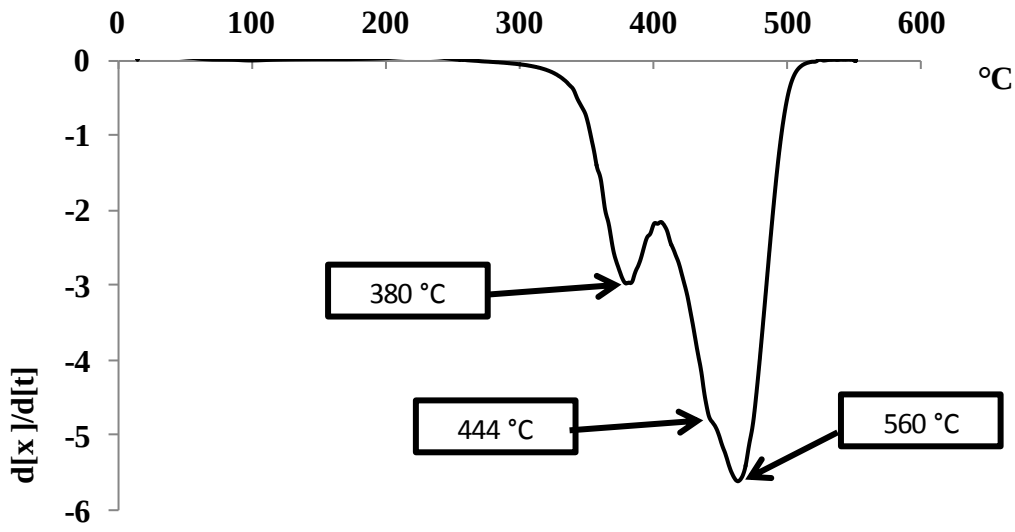


Figure 2-21, DTG of stndard Rubbers Mixture 3

T_{max} shift for SBR is also noticeable when it is in mixture of standard rubbers comparing to that one when it is alone or in tire. While NR T_{max} isn't exposed to any shift. This could be explained by taking into account that NR started to degrade before other rubbers. In this case no side degradations; coming from other rubbers (side reactions); affect its decomposition, while other rubbers (SBR and BR) degradations happen at time when other degradation process have taken place; SBR degrades at the time that NR has already happened, while when BR starts to degrade, both NR and SBR have already commenced. This could be proven by the ranges of degradation of all rubbers in the table 2-4, that all rubbers share a big thermal range of degradation even if some start before other.

As the pyrolysis process included complicated reaction with endo and exo thermic. Then the decomposition of a rubber is affected widely with the other ones, especially when they start to degrade before it. That is what happens in tire pyrolysis causing shifting in T_{max} of both SBR and BR.

Sharing the same range of degradation due to that all rubbers have mostly the same chemical bonds which are mainly C-H, C-C and C=C in aliphatic form (branches and linear, fig 2-31); in addition to small difference in SBR that it contains aromatic bonds. This should be reflected in kinetic constants which will be studied in the next paragraph.

Mixture	NR		SBR		BR	
	%	T_{max}	%	T_{max}	%	T_{max}
Mix 1	21.19	380	65.97	438	12.84	462
Mix 2	26.51	376	52.29	437	21.21	455
Mix 3	42.47	380	17.37	442	40.16	460
	100 (individual)	380	100 (individual)	433	100 (individual)	475
	In tire	380	In tire	428	In tire	460

Table 2-5, Change of T_{max} depending on Rubber concentration

Chemical structure of each rubber, vulcanization level, rubber combination method (intramolecular liaison) could affect the phenomena of T_{max} shifting and the range of thermal degradation sharing.

2-III.4.2 Quantitative composition determination

Quek et al [5] estimated the masses of each individual component from the graph $\frac{dM}{dT}$ vers T. The mass of each component changed proportionally with HR change for HR = 10, 20, 30, 40 and 50 °C/min. the fractional mass of NR, SBR and BR changed (11.6, 11.1, 16.9, 18.5 and 26.6), (21.6, 22.6, 18.4, 41.9 and 19.5) and (51.3, 50.7, 46.4, 32.9 and 24.7) respectively.

In addition, Quek et al [5] found that with HR increment, a thermal lag happening in arising an additional peak at the end of the graph.

As it is shown in table 2-4 and has mentioned above, pyrolysis of rubbers in the tire is very interfered and overlapped with each other; the pyrolysis process of all rubbers in the tire takes place in parallel at the same time [21]. So, quantitative determination of individual rubber in the tire is difficult to be achieved precisely. But what could be done is: determination the type of rubbers and their entire quantity.

2-IV Kinetic study

2-IV.1 Introduction

Although several fundamental studies on pyrolysis of scrap tires have been carried out over the years, the mechanism involved in the pyrolysis process has not been completely understood yet [5].

The importance of kinetic study comes from the requirement of understanding the treatment of material behavior before designing lab-scale or industrial unit. Integrating a pyrolysis unit in a laboratory or industrial scheme doesn't only require the powering up elements (oil, gas and electricity) to be covered. But also a sound model that will predict residue amount, products and heat, and energy balance parameter is paramount for the operation of such a plant.

Current modeling efforts have focused only on the chemical reaction rates, which implicitly assume a reaction rate limiting mechanism in the pyrolysis of tyres [1,5,29]. Modeling the kinetics of the tires pyrolysis provides insights into the mechanisms responsible for pyrolysis process and predicts potential difficulties in the pyrolysis reactor.

Quek et al [5], proposed model with assumption that tires compose of extender oil, NR and manufactured rubbers (BR and SBR). Each of these components follows the basic Arrhenius-type rate equation with the first order reaction in the pyrolysis process. Thus, a more realistic and popular approach is to model each major component of tire separately.

In order to maximizing the desired products and minimizing the residual fraction, Al-Salem et al [3] undertook a kinetic approach to evaluate the rate constants and estimate the product based on a first order (n=1) thermal cracking reaction. In addition, they put another assumption of one side irreversible reaction for polyisoprene and butadiene which present in the scrap tyres, as shown in the following scheme (scheme 2-1):

$$[PI] \rightarrow \begin{bmatrix} \overrightarrow{k_1} & [A] \\ \overrightarrow{k_2} & [L] \\ \overrightarrow{k_3} & [G] \\ \overrightarrow{k_4} & [C] \end{bmatrix}, [L] \rightarrow \begin{bmatrix} \overrightarrow{k_5} & [A] \\ \overrightarrow{k_6} & [G] \end{bmatrix}$$

Scheme 2-1, cracking steps of isoprene [3].

The thermal cracking model shows first order primary cracking of poly isoprene (PI) in scrap tyres to aromatic [A], liquids [L], gas [G] and char residue [C] with corresponding rate constants k_1,k_2,k_3 and k_4 respectively. And the secondary side reaction of liquids to aromatic [A] and gas [G] with constants k_5 and k_6 respectively.

These reactions could be expressed by the following equation (equation1):

$$\frac{dX_i}{dt} = -X_i(k_1 + k_2 + k_3 + k_4) \qquad (1)$$

$$\frac{dX_i}{dt} = -X_i k_i \qquad (2)$$

Where X_i is the fraction of non degradable of polymer (tires).

When t=0, X_i =1.

Actually, when polymers (tires) are subjected into thermal cracking; mainly under the influence of a fixed heating rate; they undergo complicated process, such as random chain scission, end chain scission, chain stripping, cross linking and coke formation[1,3].

While, the basic rate equation of weight loss of polymer described as follow [1-3, 5]:

$$\frac{dX_i}{dt} = -k(1 - X_i)^n \qquad (3)$$

$$k = Ae^{\frac{-E_a}{RT}} \qquad (4)$$

From equations 3 and 4, the equation 5 is obtained

$$\frac{dX_i}{dt} = -A(1-X_i)^n e^{\frac{-E_a}{RT}} \qquad (5)$$

Where:

X_i : is the pyrolysable fraction of polymer.

A : is the Arrhenius pre-exponential factor (s^{-1}).

k : Reaction rate constant (s^{-1}).

E_a : Activation energy ($Jmol^{-1}$)

n : Order of reaction.

R : General gas constant 8.314 $Jmol^{-1}.K^{-1}$.

T : Temperature K.

$$X_i = \frac{W_0 - W_i}{W_0 - W_\alpha} \qquad (6)$$

Where W_0 is the initial sample weight, W_i is the sample weight at time t_i, and W_α is the mass residue at the end of pyrolysis

Compensation of 6 in 5, with assumption that pyrolysis is reaction of first order, simplest form of this equation could be get; which applied by Williams et al [30]:

$$\frac{dW}{dt} = -Ae^{\frac{-E_a}{RT}}\left(w - w_f\right) \qquad (7)$$

$$\ln\left(-1 \times \frac{\frac{dW}{dt}}{w - w_f}\right) = \ln A - \frac{E_a}{R} \times \frac{1}{T} \qquad (8)$$

Where w is sample weight (non-pyrolysable) and w_f is the non-pyrolysable residue at the end of pyrolysis process.

$\frac{dW}{dt}$, w , w_f and T are all given by incorporated software of TGA . Plotting left term of equation 8 against $\frac{1}{T}$, the value of E_a and A could be gotten from slope and intercept values of obtained line, respectively.

Some postulates could be found in the literatures survey; it is very important to be taken into account or discussed in the results; which are:

1- Consider the whole pyrolytic process as single reaction proceeding in two stages, the first stage attributes into lower molecular mass compounds. While, aromatic and heavier hydrocarbons release in the second [1, 5, 28],
2- Pyrolysis process is a multi-stage/multi-components degradation phenomenon; the first stage is attributed to extender oils and softeners, while the other stages are attributed to tires' components NR, SBR and BR. thus a more realistic and popular approach is to model each component of the tire separately as each component is represented by a peak in the DTG curve [5,29].
3- Some researchers focused on chemical reactions rates, which implicitly assume a reaction rate limitation mechanism in the pyrolysis [4]. While other, assume that tire composes of oil and plasticizers, NR, SBR, and BR, and each component follows the Arrhenius-type rate equation with the first order of reaction; and sometimes the activation energy is fixed and unique for each component [5,29].
4- As the particle size is small enough (less than 0.1 mm in this study), the effect of mass and heat transfer is avoided (ignored) [29,30].

2-IV.2 Methodology

Kinetic study in this work will be divided in three stages as shown in figure 2-22. Each stage includes different compound or raw materials; which is reflected in different objective. These stages are:

I. Kinetic study of individual standard Rubbers (NR, SBR and BR). The objective of this stage is to have insight into the thermal behavior of each rubber individually.
II. Kinetic study of mixtures of standard rubbers added together without additives and cross-linking between them. The objective of this part of study is to have insight into the interference and overlapping between Rubbers.
III. Kinetic study of tire with different conditions of HR and FR. The objective of this stage is to have a closer look about the thermal behavior

of tires, effect of inter and/or intra combination between rubbers themselves and thus between tires and additives (vulcanization and cross-linking).

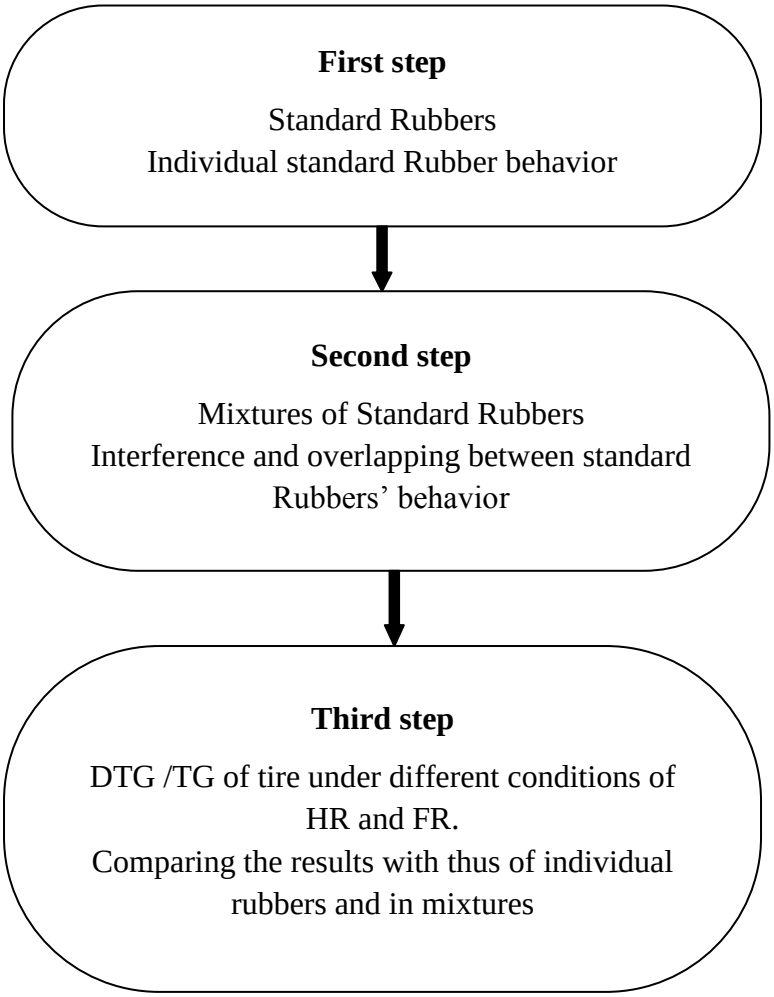


Figure 2-22, Methodology of kinetic study.

Final decision on the behavior of each studied step (individual Rubber, mixture of Rubbers and tire) will be upon the Ea and A values.

2-IV.3 Result and discussion

2-III.3.1 First step: individual standard rubbers

Equation 8 is applied on DTG curves of individual standards rubber, HR =5, FR=5 and T_{max} = 500°C. Energetic behavior of each rubber individually is showed in figure 2-23:

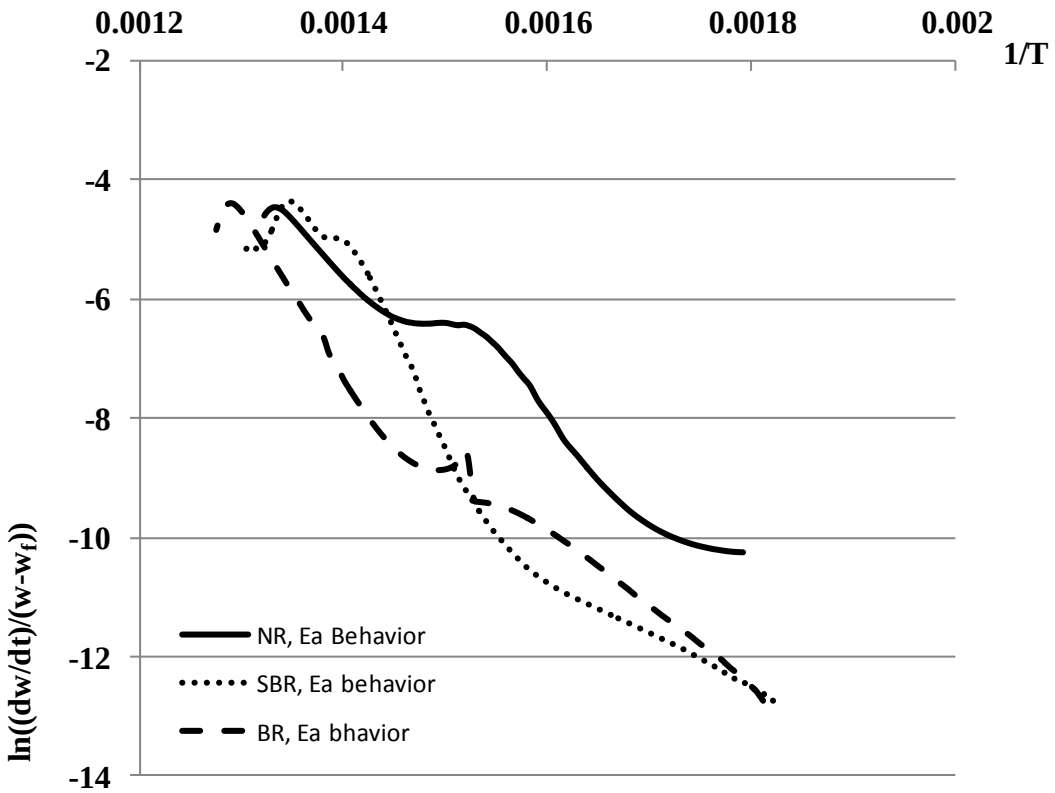


Figure 2-23, Ea behavior of individual rubber.

It is clear from figure 2-23 that the energetic behavior of each individual rubber isn't linear all over the degradation range. While it has many sub-thermal degradation zones where the linearity is good. Each separated zone (where the slope rises up) has its own different slope (Ea), intercept (A) and thermal rang. Figure 2-24 shows the NR energetic curve in order to clarify it in more details.

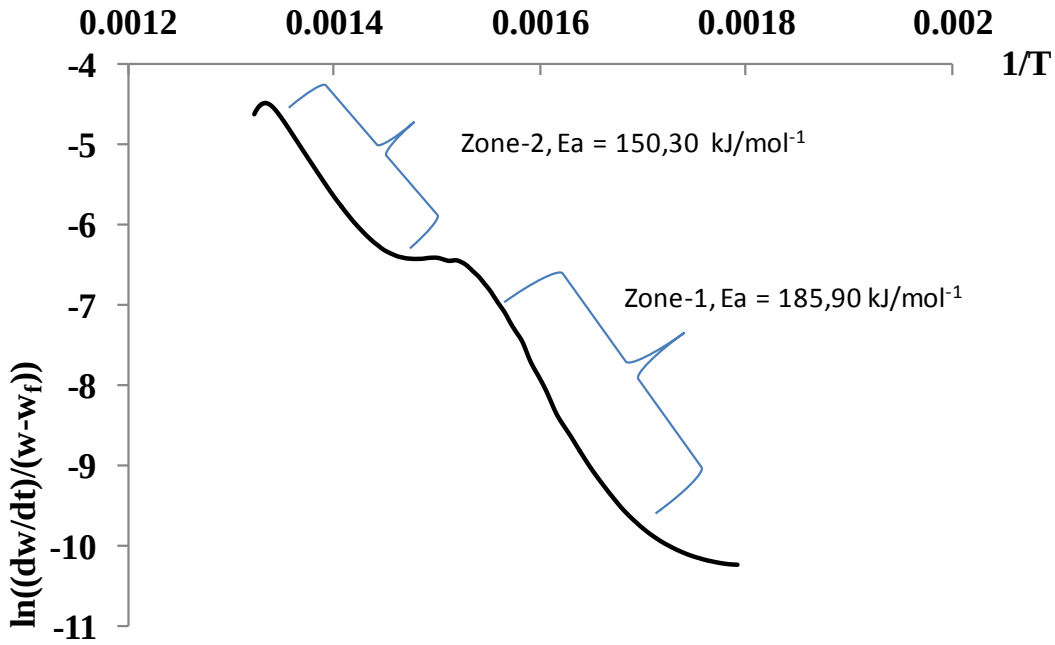


Figure 2-24, NR energetic behavior.

The linearity (fit of curve $R^2 > 0.99$) of both zones (1 and 2) is shown in figures 2-25 and 2-26 respectively.

As both zones belong to the same rubber; it means that there isn't any external interference (come from another components); the different energetic zones could be related to the different chemical bonds existing in the rubber structure (fig 2-31).

Energetic zones of each rubber with the corresponding values of Ea and A are showed in table 2-6. T_s and T_e are the temperature of beginning and end of each zone respectively; W_s and W_e are the weight of non-pyrolysable part at the beginning and the end of each zone respectively; Ea activation energy; A pre-exponential factor.

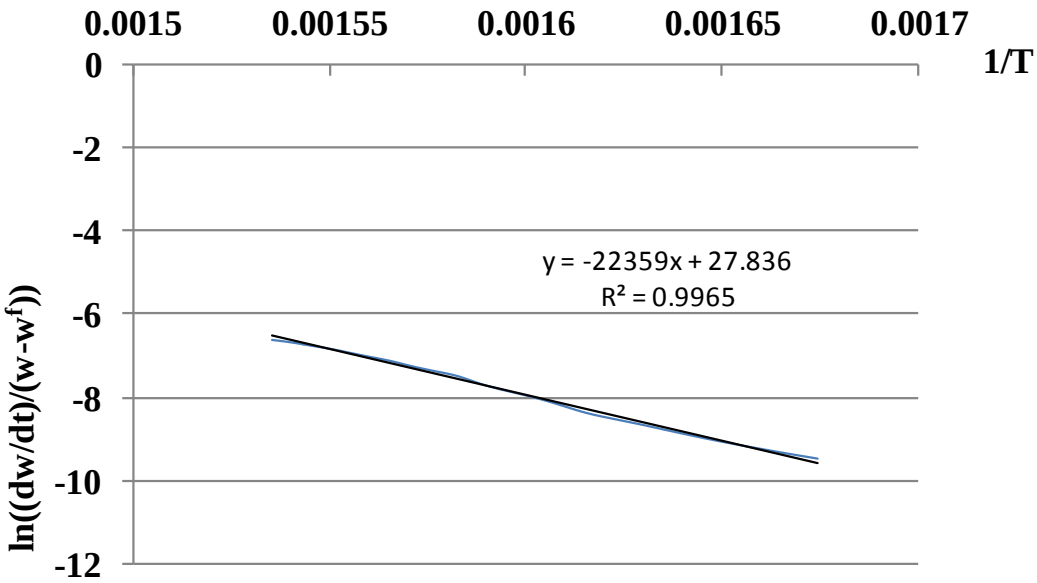


Figure 2-25, Ea behavior of NR, Zone-1.

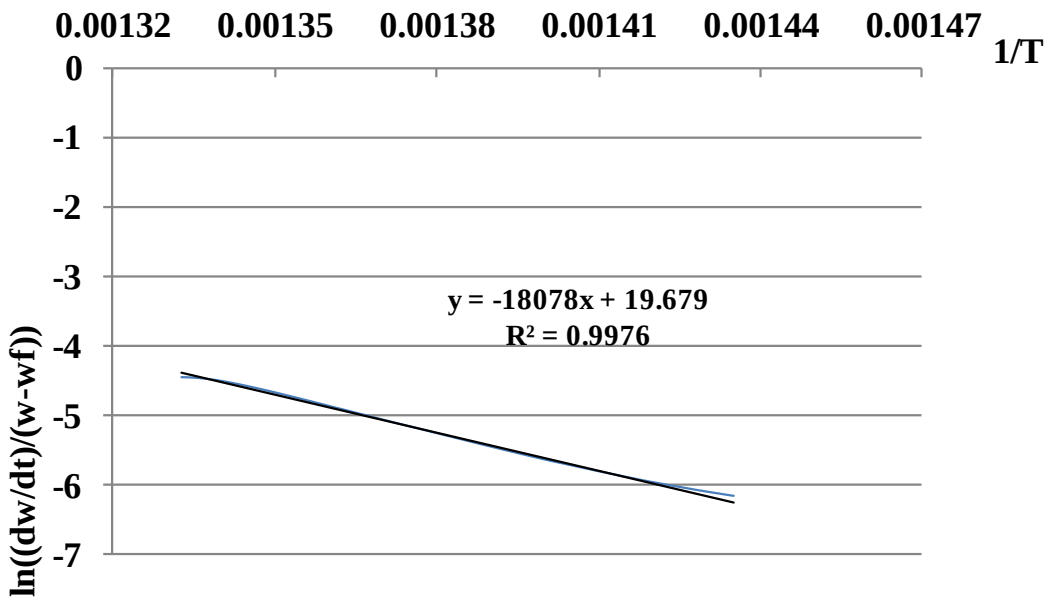


Figure 2-26, Ea behavior of NR-Zone-2

The overall degradation range of all Rubbers is the same; it starts at around 280°C and ends at around 500°C. But the difference between them is in internal sub-degradation (energetic) zones.

Rubber	Zone	T_s (°C)	T_e (°C)	ΔT	W_s (mg)	W_e (mg)	ΔW (mg)	ΔW %	Ea (Kj/mol^{-1})	A (S^{-1})
NR	General	285	483	198	88.19	2.16	86.03			
	1	328	376	48	86.11	65.77	20.34	46.64	185.89	1.22E+12
	2	425	477	52	25.85	2.58	23.27	53.36	150.30	3.52E+08
SBR	General	276	497	221	93.83	1.61	92.21			
	1	276	355	79	93.83	92.93	0.90	1.41	71.81	21.5
	2	387	436	49	91.14	35.53	55.61	87.72	318.14	1.72E+21
	3	453	465	12	10.66	3.77	6.89	10.87	185.62	1.62E+11
BR	General	279	500		107.58	2.04	105.54			
	1	283	367	84	107.56	104.64	2.92	3.18	105.21	3.20E+04
	2	420	497	77	95.74	7.06	88.69	96.82	231.60	5.94E+13

Table 2-6, energetic Zone of each individual Rubber.

Actually the energetic zones overlapped for all rubbers, especially those for both NR and BR; even that the majority of degraded mass under 380°C belongs to NR, but there is still degradation of all rubber. In addition the degraded mass over 420°C belongs to the three rubbers in considerable massive percentage for all of them. This disagrees with assumption put by many researchers (indicated above-kinetic study paragraph) that rubbers decompose separately and independently with little interference between them. This overlapping (interference) could be due to the similar chemical bonds that all rubbers contain them; C-H, C-C and C=C (fig 2-31).

The main distinguish Ea value is for SBR, this could be related to the aromatic ring available in its chemical structure. Aromatic ring is very difficult to be cracked. In addition it increases the dissociation enthalpy of bonds attached with it, Table 2-11.

To well understand the overlapping phenomenon, second step of rubber mixtures will be studied.

2-IV.3.2 Second step: mixture of standard Rubbers

Mixture of standard rubbers, mentioned in the paragraph 2.II.5, has been studied. Their energetic behavior curves are showed in the following figure 2-27:

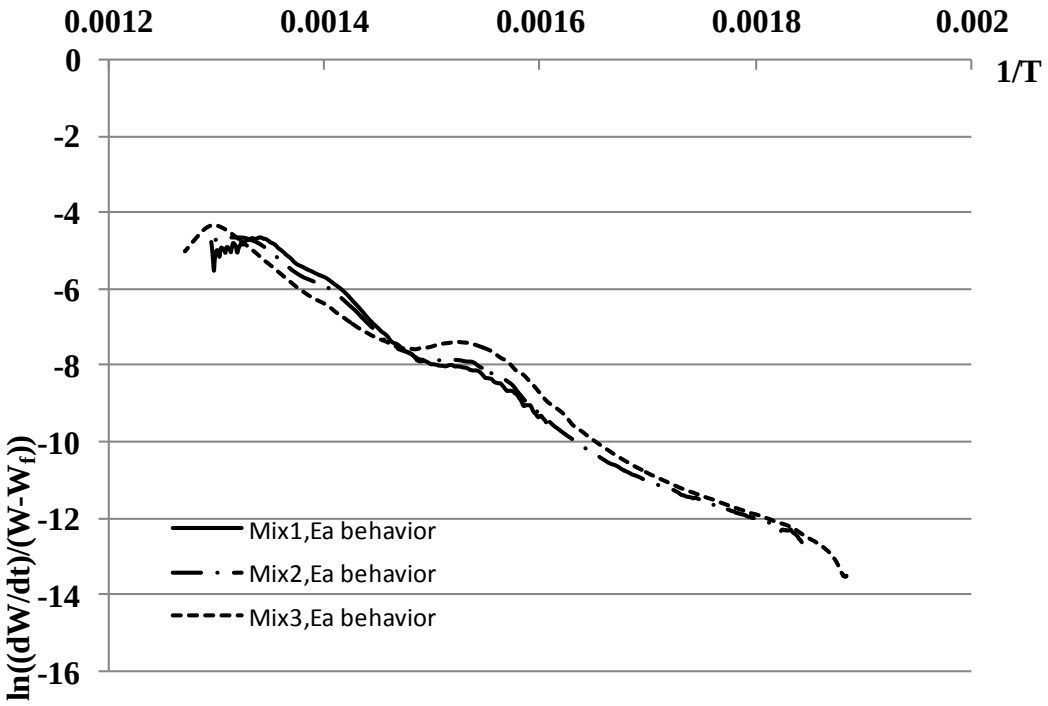


Figure 2-27, Ea behavior of different mixtures of standard rubbers.

It is obvious that the behavior of the third mix is different from those of the other two. The third one contains only two distinguished energetic zones, while the other two contain three distinguished energetic zones. The percentage of SBR is remarkable in the first and second while it is low in the third. It means that the presence and the percentage of SBR in the mixture (tire) play very significant effect on the energetic behavior of tire during the pyrolysis. The properties of each mix are showed in table 2-7.

It is clear from the previous table (2-7), that the presence of many rubbers together affect the kinetic parameters (Ea and A). This could be due to few reasons as:

1) The interaction between the produced volatiles of all Rubber. Some of these reactions are endothermic while the others are exothermic. This will be reflected in final average values of Ea and A of each zone.

2) The final average value of Ea issues from the different values of many Ea related to different parallel reactions. Each separated Ea related to different reaction or component. For example, the main degradation zone of SBR is from 380°C to 440°C with Ea=318 and $A=1.72\times10^{21}$. At this Zone, there is, as well, partial degradation for both NR and BR with different Ea and A (Ea= 185 for NR and 231 for BR). As a result, Ea value will be affected depending on kind of rubber and its percentage.

Mix	**Zone**	**T_s** (°C)	**T_e** (°C)	**ΔT**	**W_s** (mg)	**W_e** (mg)	**ΔW** (mg)	**ΔW** (%)	**Ea** (Kj/mol^{-1})	**A** (S^{-1})
Mix 1 NR = 21.19% SBR = 65.97% BR = 12.48%	General	349	499	150	98.9	2.4	96.5			
	1	350	375	25	98.9	94.3	4.5	8.7	172.0	2.47E+10
	2	400	438	38	85.1	47.0	38.1	73.1	224.0	9.83E+13
	3	455	467	12	22.0	9.6	12.4	23.7	200.3	1.18E+12
Mix 2 NR = 26.51% SBR = 52.29% BR = 21.21%	General	269	500	231	96.3	2.0	94.2			
	1	280	368	88	96.2	91.1	5.1	8.8	126.8	3.64E+06
	2	402	438	36	78.9	48.9	30.0	51.7	202.9	1.92E+12
	3	451	473	22	31.5	8.7	22.8	39.4	188.0	1.17E+11
Mix 3 NR = 42.47% SBR = 17.37% BR = 40.16%	General	257	514	257	99.7	1.1	98.6			
	1	330	370	40	98.7	90.7	8.0	11.3	212.8	9.81E+13
	2	420	495	75	65.4	2.5	62.9	88.7	183.5	6.63E+09

Table 2-7, energetic behavior of different mixtures of standard Rubber.

In addition to the kind of rubber, method of cross-linking and the available additives could, as well, play an essential role in the kinetic behavior of tire. This leads us to study the behavior of tire to see what more information could be added.

2-IV.3.3 Third step: Tire study

Applying the same conditions which have been applied on individual and mix standards; HR=5, FR=5, T_{max}=500°C. Energetic behavior of tire is showed in figure 2-28:

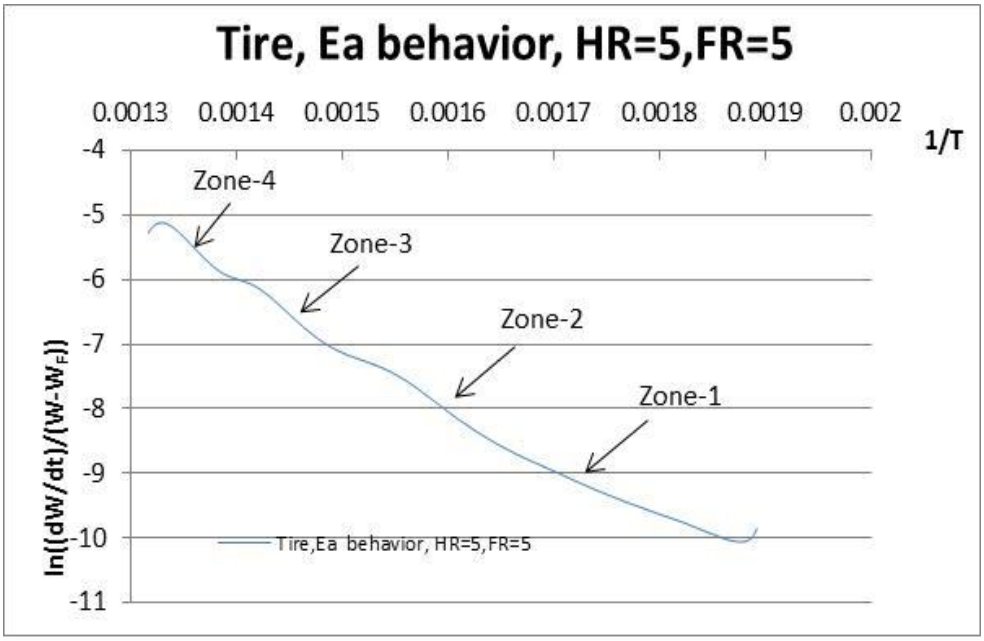


Figure 2-28, Ea behavior of tire pyrolysis, HR=5, FR=5

It is noticeable that the number of energetic zones of tire has increased one zone relatively to those of individual or mixed standards. The thermal, massive and energetic properties of each zone are showed in table 2-8:

Tire, HR=5, FR=5									
Zone	**T_s** (°C)	**T_e** (°C)	**ΔT**	**W_s** (mg)	**W_e** (mg)	**ΔW**	**ΔW** %	**Ea** (Kj/mol^{-1})	**A** (S^{-1})
General	255	486	231	99.62	41.91	57.71			
1	261	341	80	99.34	93.87	5.47	15.35	56.82	1.45E+01
2	341	368	27	93.85	88.04	5.81	16.30	99.95	7.28E+04
3	401	432	31	76.37	60.95	15.42	43.25	117.71	1.20E+06
4	448	474	26	52.95	44,00	8.95	25.10	132.14	1.17E+07

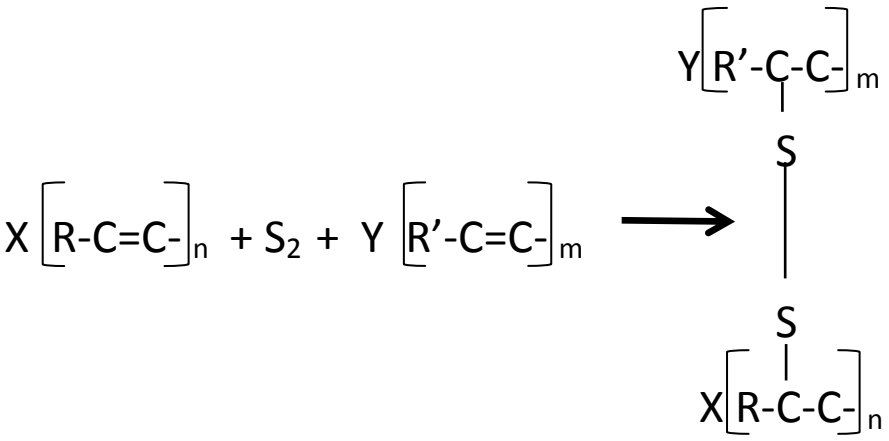
Table 2-8, kinetic parameters, thermal and massive properties of tire pyrolysis. HR=5, FR=5, T_{max}=500°C.

The additional zone (first zone in the curve), which stretching between 261°C and 340°C; interferes partially with the first zone in all rubbers and their mixture. Its Ea = 56 Kjol/mol^{-1} is lower, relatively in considerable amount, than the other

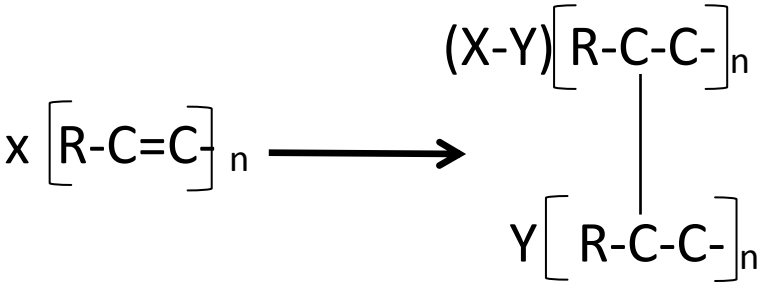
zones (in the tire or in standards). As the only paramount difference in chemical structure between tire and individual standard rubbers; either individually or in mixture; is the vulcanization process in addition to some additional additives. This zone could be related to the decomposing of some additives and sulfur bonds as C-S and S-S. Taking into account that the sulfur bonds are the weakest between other ones existing in the tire structure; The bond dissociation enthalpy of C=C, C-C, C-H, C-S and S-S are 145, 83 , 99, 65 and 54 $Kcal.mol^{-1}$ respectively (table 2-11) [32]. Additives released at 250°C and its percentage in the tire doesn't exceed 5% [1,29]. Its percentage proportionally into total pyrolysable quantity is ≈ 9% and is ≈ 15% into pyrolysable quantity in the energetic zones. This means that there is another sources for mass loss in this energetic zone else of the additives, the most probable source is the cracking of sulfur bonds (C-H cracking is coincided with sulfur bond cracking as H_2S is produced).

The other three zones accord with those of standards (either in individual form or in mixture). But they differ dramatically in kinetic parameters (Ea + A).

An explanation to this difference could be related to the modification in the chemical structure of rubbers between the two states when they are separated to those when they are cross-linked in tire. On one hand, as the cross-linking takes place on the double bond of carbon C=C, it (double bond) is replaced by two simple one; the new simple bond could be either C-C or C-S (equations 9 and 10). Both kinds of new simple bonds have lower dissociation enthalpy of the double, table 2-11. On the other hand, the goal of cross-linking is to increase the rough and hardness of rubber, this could demand more energy to be dissociated. And under the condition of the present work, the introduced energy isn't sufficient else for cracking some limited bonds. Then, the calculated value related to these weak cracked bonds.



Eq 9; Vulcanization



Eq 10; Cross-linking

To make sure about the both previous hypotheses, the pyrolysis will be studied under different conditions of HR.

2-III.3.4 Heating Rate effect

Under constant flow rate of 5mL/min of inert gas (nitrogen) and heating up to 500°C. Heating Rate changed between three values 1, 5 and 9 °C/min. The energetic behaviors of all cases are showed in figure 2-29.

2-IV.3.4.1 Results and discussion

It is clear from figure 2-29, that the energetic behavior of tire pyrolysis is dramatically different when HR is changed. The intrinsic difference is between HR=1 from one side and other two values of HR (5 and 9) from another side. The difference takes place, especially, in thermal degradation and number of energetic

zones. To have a good insight into these differences, table 2-9 shows their properties.

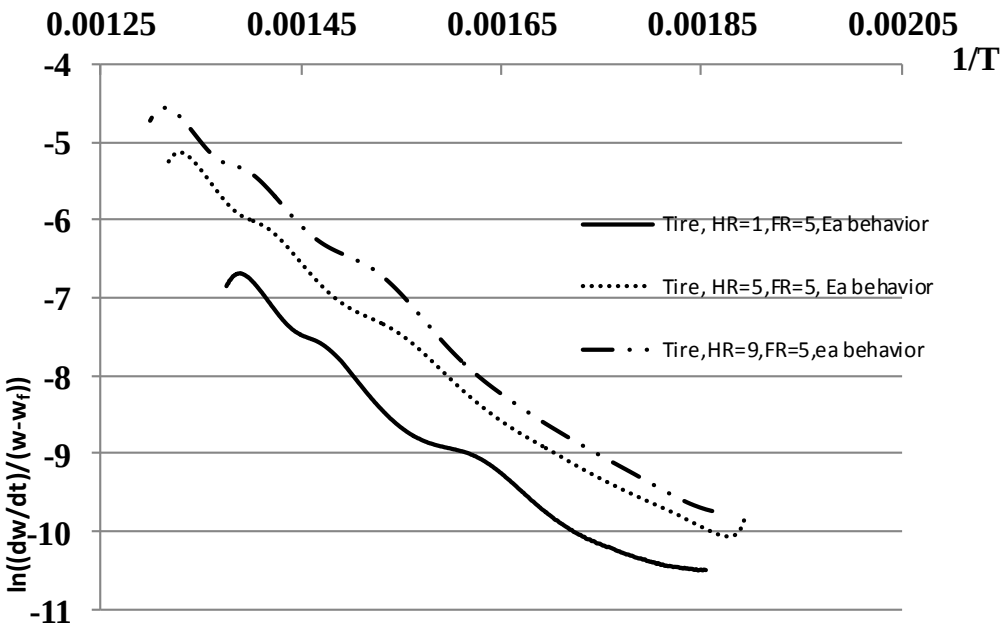


Figure 2-29, Tire Ea behavior with different HR values (1, 5, 9), FR = 5.

First of all, with HR=1, above ≈ 450°C, there is no more reaction (degradation) as there is no more energetic phenomenon appears; the mass loss appears in the DTG curve could, in this case, related into evaporation process. While with other two situations, they continue to above 480°C. This indicates that the mechanism and the quality of pyrolysis products change in a paramount way depending on HR value.

Mix	Zone	T_s (°C)	T_e (°C)	ΔT	W_s (mg)	W_e (mg)	ΔW	ΔW%	Ea (Kj/mol)	A (S^{-1})
HR=1 FR=5	General	266	453	187	94.87	40.82	54.05			
	1	307	340	33	90.49	83.65	6.84	30,83	88.62	4.13E+04
	2	376	394	18	71.59	63.54	8.05	36,32	124.60	1.20E+06
	3	421	443	22	49.95	42.66	7.29	32,85	134.18	7.58E+06
HR=5 FR=5	General	255	486	231	99.62	41.91	57.71			
	1	261	341	80	99.34	93.87	5.47	15.35	56.82	1.45E+01
	2	341	368	27	93.85	88.04	5.81	16.30	99.95	7.28E+04
	3	401	432	31	76.37	60.95	15.43	43.25	117.71	1.20E+06
	4	448	474	26	52.95	44.00	8.95	25.10	132.14	1.17E+07

HR=9 FR=5	General	264	497	233	102.32	41.57	60.75			
	1	274	330	56	102.07	99.13	2.94	11.75	61.63	5.17E+01
	2	347	369	22	97.28	92.50	4.77	19.08	119.15	4.17E+06
	3	415	438	23	73.54	61.57	11.97	47.84	119.42	2.52E+06
	4	463	481	18	49.28	43.94	5.34	21.33	130.10	9.96E+06

Table 2-9, kinetic parameters and thermal degradation range of tire energetic zones for different HR values (1, 5 and 9) C/min; under constant FR =5mL/min.

With HR=5 or 9, there are four energetic zones, while they are only three with HR=1. First zone in both cases HR=5 and HR=9 doesn't belong to any distinguished degradation region in DTG curves. In addition, its Ea is relatively low 56 Kjol/mol and 61 Kjol/mol respectively. This could be related to that when high HR is introduced, they support higher amount of energy and heat; this can lead to sudden thermal shock that the material is subjected to. This thermal shock could cause rapid change in the physical state of material (from solid into gel or liquid state). Physical state change is endothermic phenomenon and could be respect Arrhenius equation.

Secondly, as has been showed in previous thermogram of (DTG curves), when HR increases the wide of degradation range extends, in addition to the shifting in the degradation zone and T_{max}. The same takes place here, there is shifting in the energetic zones and range of its linearity, that the zones with case HR=1 related to the zones number 2, 3 and 4 respectively in both cases HR=5 and HR=9. Each zone finishes at the end of degradation peak where the rate of degradation is maximum (inflexion point after the rate of degradation is maximum).

Kinetic parameters (Ea and A) of zones in all HR cases are close to each other, this means that the same cracking reactions take place in the same zone whatever the HR. But the big difference between the corresponding zones in each HR case is situated in the thermal range and decomposed mass percentage ΔT and ΔW. Theoretically, in HR=1 case, the cracking reactions take their sufficient time that all probable cracking happened, while with other two cases, as the speed of heating is faster than the cracking time, some of these crackings are shifted the next zone. This could lead to change in the quality of product and side reactions in the vapor phase. This should be assured in the lab-scale work.

2-IV.3.5 Flow Rate effect

With constant HR=5, and T_{max} of degradation 500°C, ATG has been done under different nitrogen flow rate which are FR= 5, 50 and 95 mL/min. The energetic curves are showed in figure 2-30.

It is clear that there is no significant difference between the three curves. Their properties of kinetic parameters, thermal and massive ranges are showed in table 2-10.

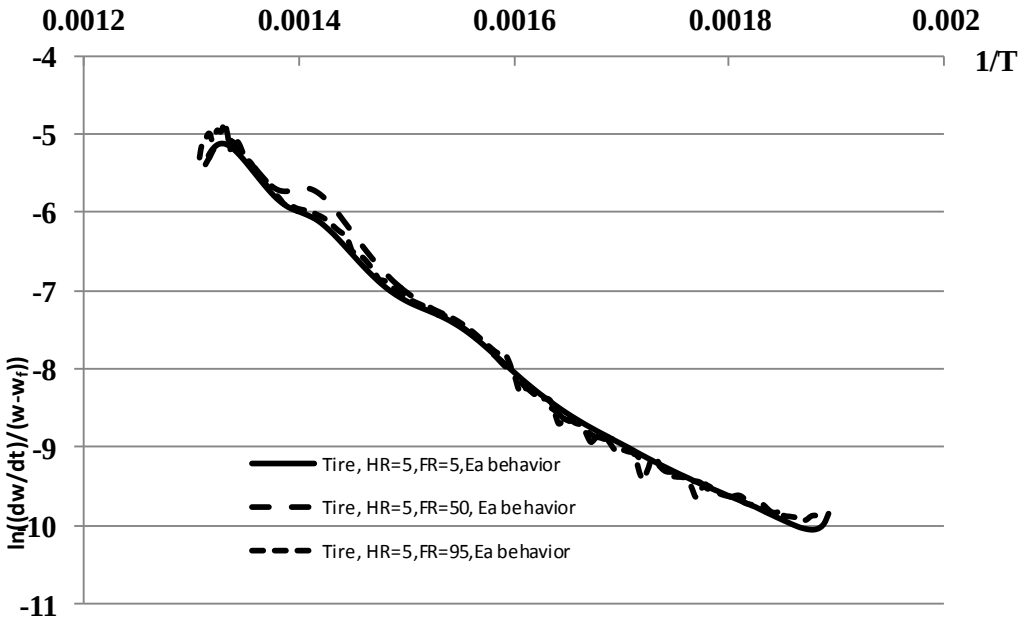


Figure 2-30, Tire Ea behavior with different FR values (5, 50, 95), HR = 5).

Condition	Zone	T_s (°C)	T_e (°C)	ΔT	W_s (mg)	W_e (mg)	ΔW	ΔW %	Ea (Kj/mol)	A (S^{-1})
HR=5 FR=5	General	255	486	231	99.62	41.91	57.71			
	1	261	341	80	99.34	93.87	5.47	15.35	56.82	14.5
	2	341	368	27	93.85	88.04	5.81	16.30	99.95	7.28E+04
	3	401	432	31	76.37	60.95	15.43	43.25	117.71	1.20E+06
	4	448	474	26	52.95	44.00	8.95	25.10	132.14	1.17E+07
HR=5	General	267	491	224	91.25	36.16	55.08			
	1	267	338	71	91.25	86.72	4.53	14.51	50.91	2.22E+01

FR=50	2	338	376	38	86.70	81.16	5.54	17.73	108.78	4.50E+05
	3	400	431	31	69.59	51.86	17.73	56.73	143.10	1.62E+08
	4	457	473	16	41.21	37.76	3.45	11.04	137.51	2.56E+07
HR=5 FR=95	General	258	492	234	96.92	39.63	57.29			
	1	258	360	102	96.92	94.55	2.37	8.14	58.81	2.22E+01
	2	395	438	43	76.36	55.03	21.33	73.30	111.71	4.50E+05
	3	453	470	17	48.72	43.32	5.40	18.55	149.06	1.62E+08

Table 2-10, kinetic, thermal and massive properties of tire pyrolysis under fixed HR=5 °C/min and different FR values 5, 50 and 95 mL/min.

2.IV.2.5.1 Results and discussion

Depending on table 2-10, both cases FR = 5 and 50 differ considerably from this of FR=95. First of all, with FR = 5 and 50, there are 4 energetic zones, while there are only three ones with FR=95.

Comparing between FR=5 and FR=50, the difference is very small in all characterization, thermal range, mass loss percentage and kinetic parameters. Even Ea increases lightly in FR=50 zones comparing to corresponding ones in FR=5.

Going to FR=95, there are only three zones, the first zone is considered as merged zones 1+2 in other cases. Its thermal degradation range (102 °C) is similar to those with other cases; for FR=5 (80+27) =107°C, for FR=50 (71+38) = 109°C. While, Ea value 58.81 is lower than their average values; FR=5 (56.82+99.95)/2=78.39 Kjol/mol, FR=50 (50.91 + 108)/2=79.46 Kjol/mol). In order to find good explanation to this result, return back to figure 2-13 that the direction of inert gas is against the produced vapor in the pyrolysis crucible. In addition, the volume of empty part of crucible is very bigger than the raw material volume. This means that with FR=95, high pressure is born over the raw materials in the crucible reducing the going out quantity of the produced vapor out the crucible. Then, the produced volatiles stay longer time in the crucible at long of temperature increase, giving more probability to side reactions, some of this side reaction could be exothermic ones with negative Ea; especially when there are association reaction, reducing the quantity of going out volatile and the average Ea.

In zone-2, in case of FR=95, which corresponds to zone-3 in both cases FR= 5 and 50, the same thermal range nearly in the three cases; while the mass loss

percentage is increased respectively with FR increase. While For Ea value, it is higher with FR=50 than in the others. Even in both cases FR=5 and FR=95, Ea is the same.

An acceptable explanation, the increase of mass loss percentage is due to that the remained non-evaporated vapor from previous zone, in each case, in addition to the new produced vapor due to longer residence time and side reaction, going out at this step as the temperature is increased as well. To rely that with the big difference in Ea, especially that with FR=50, as the pyrolysis mechanism is so complicated and not clear and understood. There is possibility to huge number or cracking and additional reactions with endo- and exo- thermic phenomenon. This puts us in front of very complicated matter that pyrolysis is a very sensitive process that could be widely influenced with the conditions subjected into.

For last zones; zone-3 in case of FR=95, zone-4 in other two cases, all of them have the same thermal range, while the mass loss percentage is reduced when the FR increase. It is as normal event as the majority part of tire have been gone out in the previous zones in all cases. The remained heavy components, demanding high temperature to go out the crucible, increase with applied pressure over it.

The respective increase of Ea with pressure increment is predicts as the evaporation process becomes more difficult and energy demanded.

Finally, the FR affects well the pyrolysis process which is very sensitive to the conditions applied on. But stay to remember that the direction of inert gas in the TG mode is opposite to that one in lab-scale work where it enters inside the reactor carrying out the produced vapor reducing the residence time inside the reactor and preventing side reaction to take place. So it should be well studied at lab-scale work and its TG result couldn’t be considered as reliable one.

2-V Conclusion

C/H ratio in used tire is 12.20. It is good value to encourage the pyrolysis of available scrap tire to be pyrolysed.

DTG/TGA of tires and standard rubbers (NR, SBR, and BR) showed that used scrap tire consists of the three mentioned common rubbers. Pyrolysis ends at 500°C. Volatile percentage is around 60%. HR and FR have no effect on the volatile yield. While HR shifts up the T_{max} .

Kinetic parameters (Ea and A), thermal degradation range and its percentage of mass loss are well effected by HR and FR, this means that the mechanism of pyrolysis, which reflects in the quality and quantity of volatile products (liquid and gas), is well changed. This is very important to be taken into account in the lab-scale work in order to get the highest yield of liquid product (as it is the objective of this thesis) with the best quality depending on the characterization following EN590 standard.

Low HR (=1) showed light degradation process (slow and not rigorous), the rate of degradation is small comparing to those of HR =5 or HR =9 which are 0.60, 2.97 and 4.96 mg/min respectively. In addition the degradation stops at around 450°C when HR=1 while it continues up to 480°C with other values. This means that with low HR, only weak chemical bond (S-S, C-S, C-H with some C-C) are exposed into cracking. In this case cyclization/ aromatization reaction are reduced which reflected in good liquid properties, especially tar content.

As the direction of inert gas is different from that applied on lab-scale work, high attention should be put in mind when discuss lab-scale work result comparing with TGA.

Stay to say that the obtained kinetic parameters accord with the work of some researchers and disaccord with the other. Either they have similar conditions of HR and FR or non. Some of these results are showed in review made by Quek et al [29]. Table 2-11 exposes some of them.

Reference	A (S^{-1})	Ea ($KJ.mol^{-1}$)	remarks
Augustine Quek [5]	NR= 0.2×10^{14} - 2×10^{14} SBR = 0.01×10^{9} - 1.5×10^{9} BR = 4×10^{9} - 1.5×10^{13}	NR=207 SBR=152 BR =215	K limit mechanism in the. Reassured it. Correction of heat and mass transfer HR = [10 - 50 °C/min] Ea, Fixed, from literature
Zabanioto et al/ table 3 in reference 29/	5.1	65.6/ two much lower	Flash pyrolysis, single-stage
Mui et al/ table 3 in reference 29/	5×10^{4} - 5×10^{15}	50 -178	HR = 5
William et al [30]	$9,3\times10^{7}$- $2,1\times10^{8}$	102-8 - 142,7	HR=5

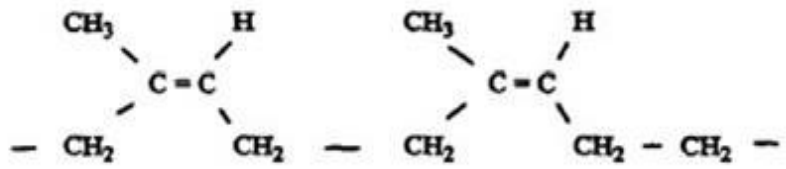
Table 2-11, kinetic parameters of tire pyrolysis of some researchers.

This is evidence that the pyrolysis process is very sensitive to the kind of raw material composition [29] and to the applied conditions of T, HR, FR...etc.

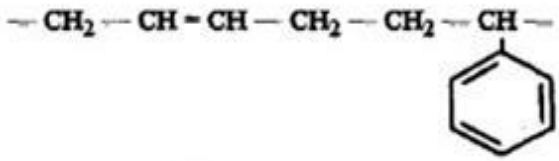
TG doesn’t give enough information about the actual pyrolysis because of the following drawbacks:

1. Force of inert gas prevents of pyrolytic products going out of the crucible easily, the pyrolytic products undertake side reaction. Especially at the end of reaction where the quantity of produced vapor became little and it hasn’t enough force pushing the volatile outside the crucible. For that kinetic parameter detection is little difficult and isn’t accurate via TG/DTG process, for that should be well determined by lab-scale process.

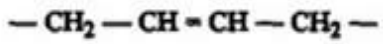
2. Weighing of remained material in the crucible takes place at higher temperature, but the sensitivity of balance as well the precise of weighing process isn't the same at long of pyrolysis process.
3. Very low mass (mg), used in TG, doesn't represent the all tire, as its composition differs between wall side and the tread.



[a] Natural Rubber (NR)



[b] Styrene-Butadiene Rubber (SBR)



[c] butadiene Rubber (BR)

Figure 2-31 , Rubber structure [30]

Bond	Bond	Bond-dissociation energy		Comment
		(kcal/mole)	(kJ/mole)	
$H_3C–H$	Methyl C–H bond	105	439	One of the strongest aliphatic C–H bonds
C_2H_5-H	Ethyl C–H bond	101	423	slightly weaker than $H_3C–H$
$(CH_3)_3C–H$	tertiary C–H bond	96.5	404	tertiary radicals are stabilized
$CH_2CH–H$	vinyl C–H bond	111	464	vinyl radicals are rare
HC_2-H	acetylenic C–H	133	556	acetylenic radicals

	bond			are very rare
C_6H_5-H	phenyl C–H bond	113	473	comparable to vinyl radical, rare
CH_2CHCH_2-H	allylic C–H bond	89	372	such bonds show enhanced reactivity
$C_6H_5CH_2$-H	benzylic C–H bond	90	377	akin to allylic C–H bonds such bonds show enhanced reactivity
$H_3C–CH_3$	Alkane C–C bond	83–85	347–356	much weaker than a C–H bond
$H_2C=CH_2$	Alkene C=C bond	146–151	611–632	about 2x stronger than a C–C single bond
HC≡CH	alkyne C≡C triple bond	200	837	about 2.5x stronger than a C–C single bond

Table 2-12, some chemical bond energy [32]

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Chapter 3
Experimental Work

3-I Introduction

Depending upon the results of DTG work in the chapter 2; pyrolytic products are well affected by the pyrolysis conditions: temperature, heating rate and flow rate. Indeed; as DTG/TGA showed; pyrolysis takes place from 300°C up to 500°C. While last peak of maximum rate of degradation appears at 460°C - 470°C. The question is: in the gap between 470°C and 500°C, what is the thermal process that it takes place? Is there any more degradation process or just evaporation process of heavy molecules? Especially the volume of crucible is too big compared to material volume. DTG/TGA analysis showed as well that the nitrogen direction is opposite direction of the produced vapor (fig 2-13). This demands more thermal energy to evaporate heavy molecules!?

The effect of the three factors has to be studied and optimized. The objective of this optimization is the production of liquid product which respects the characterization mentioned in EN590 [1].

Literature survey showed that the factors which affect the pyrolysis process; either the pyrolytic products yields or the quality of these products; are temperature, heating rate, flow rate and the gas chemical nature (inert. CO_2, N_2), residence time, particle size and pressure [2,3,4].

As the work will be done in fixed-bed batch reactor with open system at atmospheric pressure by consequence the pressure factor will not be studied.

Raw material is brought from a company specialized in scrap tire collection and shredding (cutting). Then, the company sells it in heterogeneous dimensions pieces without separation of steel and textile from rubber to be used for incineration. Separation and cutting (shredding) in more small pieces consumes more energy and time. In this case particle size will stay out of study as well.

Another term that should be considered is the heat transfer into interior layers in the tire [2-4]. As in the present work: lab-scale level, pieces of centimeter dimensions. Mass of around 1kg are used, and tire in the reactor full approximately two thirds of the reactor volume. Then, the temperature homogeneity is very important in tire pyrolysis process.

Return back to chapter 2, general noteworthy shows that big part of degradation mostly takes place at around 400°C. Then it continues to higher temperature (≈ 500°C). It is important to study the pyrolysis at each temperature value (in two levels) and to compare it with continuous slope up to 500°C.

It stays to remember that the objective of this work is to obtain good yield of liquid product with high quality following EN590. And all the calculations of products' yield based on rubber without steel.

After these aforementioned notes. The experimental work steps will be in as the following:

1) Step 1: Study the pyrolysis process at two temperature levels (400°C and 500°C) and continuously (non-isothermal) up to 500°C.
2) Step 2: Study the mixing effect on pyrolysis process in order to keep uniform temperature inside the reactor.
3) Step 3: Optimization of the pyrolysis conditions temperature, heating rate and flow rate.

3-II Step 1: Study the pyrolysis with two thermal programs

In this paragraph, experiments will be done in two thermal programs. The first consists of two phases of heating: 400°C and 500°C. The second program is a continuous heating up to 500°C. Then, a comparison will be done between the two programs in order to define which program is the best to follow. In these cases, the time of pyrolysis at 400°C should be well determined.

3-II.1 Determination of residence time at 400°C and 500°C (preliminary experiment)

A preliminary experiment will achieved to have an idea about the necessary time to keep the pyrolysis at 400°C. The judgment will be via monitoring the temperature of the going out gases (volatiles) in addition to measuring the change in the concentration of the major produced gases which are H_2 and CH_4. Sample

weight is about 200 g and the showed results are the average of triplicates. The followed thermal program is showed in Table 3-1:

Start temperature (°C)	**End temperature** (°C)	**Heating Rate** (°C/min)	**Residence at end temperature** (min)
room temperature	400	5	-
400	400	0	180
400	500	5	-
500	500	0	180

Table 3-1. Thermal program of the preliminary experiment.

3-II.1.1 Result and Discussion

Figure 3-1 shows the behavior of going out gases' temperature compared with the both temperatures: reactor and blank. While figure 3-2 shows the concentration change of both H_2 and CH_4 along of pyrolysis process.

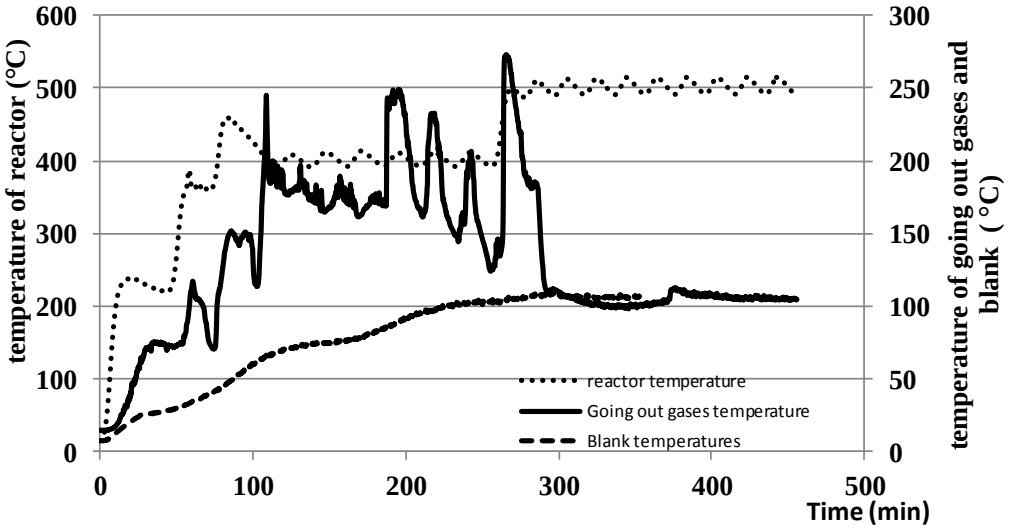


Fig 3-1, Temperature of reactor, going out gases and blank. two level program. preliminary experiment.

It is clear in Fig 3-1 that when the temperature reaches 400°C, a big rate of degradation takes places as the temperature of going out gases raises sharply. This degradation continues for few minutes to start minimizing sharply as well. This agrees with DTG results in Chapter 2. After that, as the reactor temperature fluctuates around 400°C, the going out gases temperature stays stable for 80 minutes nearly. Then, it fluctuates up and down again. This means that degradation starts again but at low rate. This degradation could be due to secondary cracking of vapor remained in the reactor or resume rubber degradation under the effect of temperature and time together. Even, if the raise up in the going out volatiles due to resumption of the tire pyrolysis. It consumes long time which is not recommended.

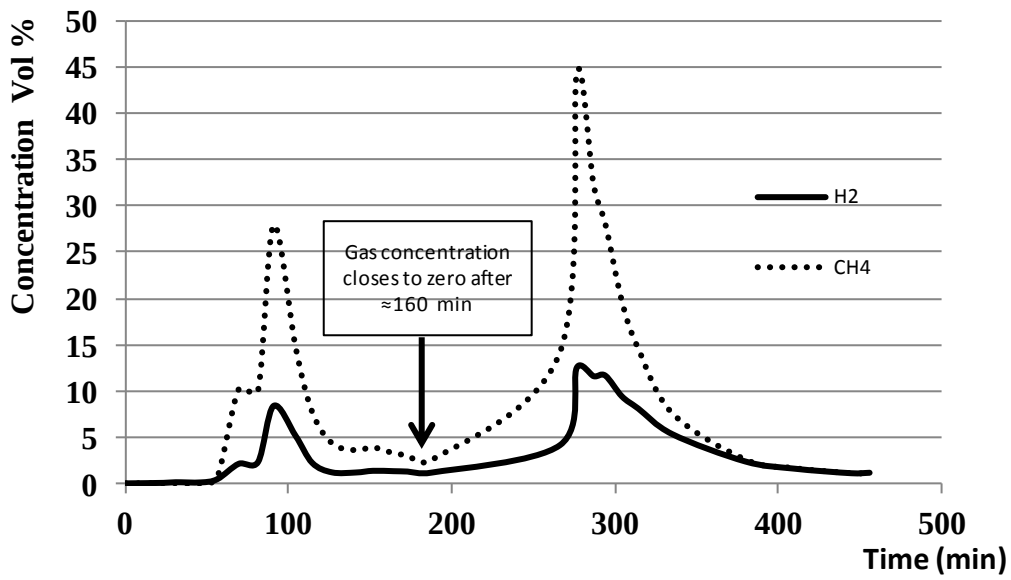


Fig 3-2, H_2 and CH_4 concentration. two levels program. preliminary experiment.

In addition, Fig 3-2 shows that the rate of fluctuated degradation is very low and close to zero. Fig 3-2 shows that 80 minutes at 400°C (160 minutes after the heating begin) is sufficient to finish the degradation (pyrolysis) at this temperature. Indeed, at 500°C, 60 min seem to be sufficient to complete the pyrolysis.

3-II.1.2 Conclusion

Pyrolysis at two levels of temperature 400°C and 500°C will be studied with residence time 80 minutes and 60 minutes at 400°C and 500°C respectively.

3-II.2 Comparison between two thermal programs - one and two levels

The objective of this part of work is to show the effect of temperature on the products yield and its quality. For this purpose, two different thermal programs E1 and E2 will be applied. The first consists of two steps to reach 500°C. Temperature raises up from room temperature (≈20°C) to 400°C with heating rate 5°C/min (it takes about 76 min). Then, it stays at 400°C for 80 minutes, it resumes its raising up to 500°C with heating rate 5°C/min as well during 20 minutes; residence time at 500°C is 180 minutes. While in the second program E2, temperature is raised up continuously up to 500°C with 5°C/min during 96 minutes, it stays at 500°C for 180 minutes. Inert gas (N_2) flow rate is 100mL/min along the process duration. They are shown in the table 3-2. In both programs, heating at 500°C will be kept for 180°C to ensure that the pyrolysis completely is finished.

Step	**First program E1**					**Second program E2**			
	Initial temperature (°C)	Final temperature (°C)	Heating rate (°C/min)	Residence time (min)		Initial temperature (°C)	Final temperature (°C)	Heating rate (°C/min)	Residence time (min)
1	room T 15- 20	400	5	76		room T 15- 20	500	5	96
2	400	400	0	80		500	500	0	180
3	400	500	5	20					
4	500	500	0	180					
	Time up to 500°C = 356 min					Time up to 500°C = 96 min			

Table 3-2. Thermal programs E1 and E2

3-II.2.1 Results and discussion

3-II.2.1.1 Thermal behavior

Figures 3-3 and 3-4 show the thermal behavior of applied (theoretical) thermal program (Program), actual reactor temperature (Reactor), volatiles–going out gases- and temperature of thermocouple which measures the temperature when there is no tire in the reactor (Blank). Blank temperature has been selected to be compared with other temperatures because it is supposed that at the end pyrolysis, there will be no more volatiles going out the reactor. Then the temperature will return back to the inert gas current temperature only.

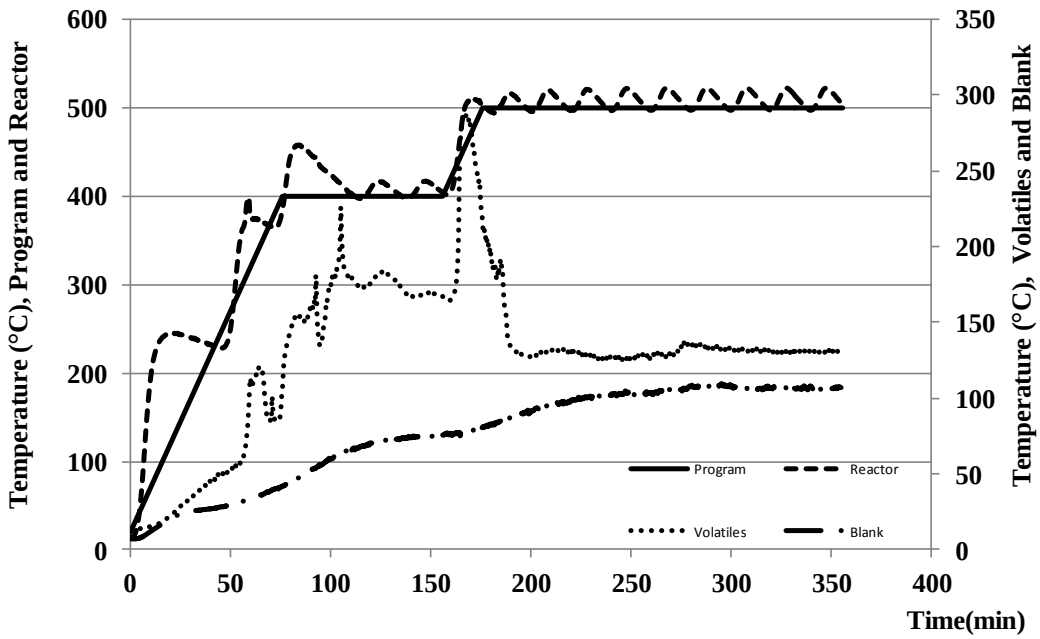


Fig 3-3, Temperatures' behaviorof E1, Program, Reactor, Volatiles, and Blank.

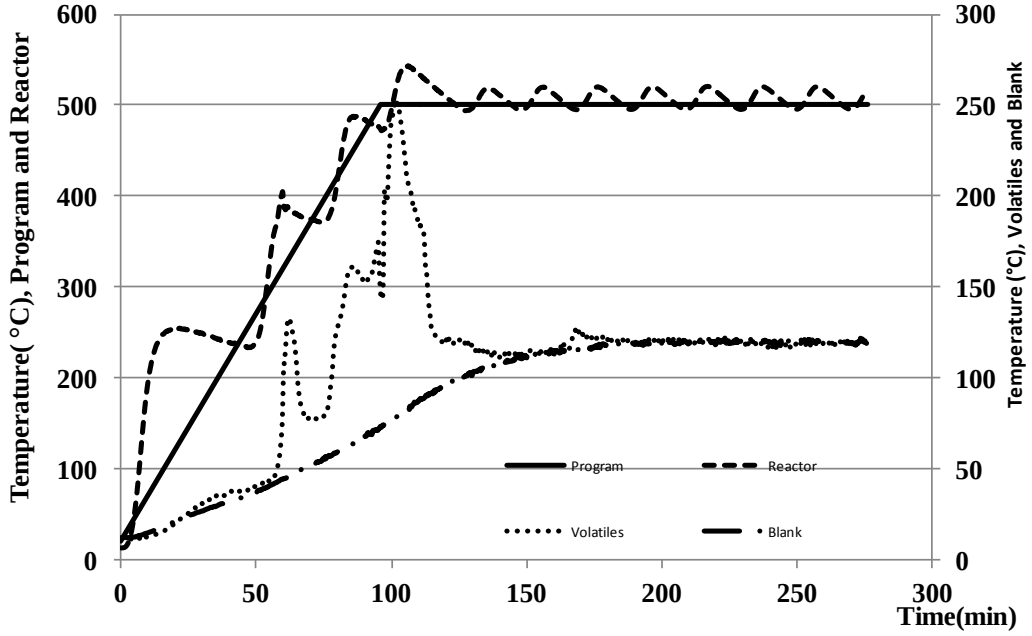


Fig 3-4, Temperatures' behaviorof E2, Program, Reactor, Volatiles, and Blank

Three valuable information could be obtained from figures 3-3 and 3-4 which are as follow:

1- Temperatures of volatiles in E1 reach higher degree (≈ 288°C) from those of E2 (≈255°C). It is shown more clearly in figure 3-5. This means that more heavy molecules are produced in E1 than from what are produced in E2. Especially if these heavy molecules are PAHs, which are not recommended in pyrolytic liquid. This could be due to secondary cracking of remained vapor in the reactor or very small quantity of volatile produced slowly at this step (T ≈ 400°C). And as the actual temperature ≈400°C isn't enough to evaporate them out of the reactor. Secondary cracking could include the three coincided reactions (dehydrogenation/ cyclisation/ aromatization) via Diels-Alders mechanism. This explains both:

   i. The continuation of gas production (especially H_2. figure 3-6); even if it is very weak; when the temperature is fixed at 400°C.

ii. And non-return back of volatiles' temperatures to the blank level as what it happens at the end of pyrolysis. this emphasizes that there is more thermal process

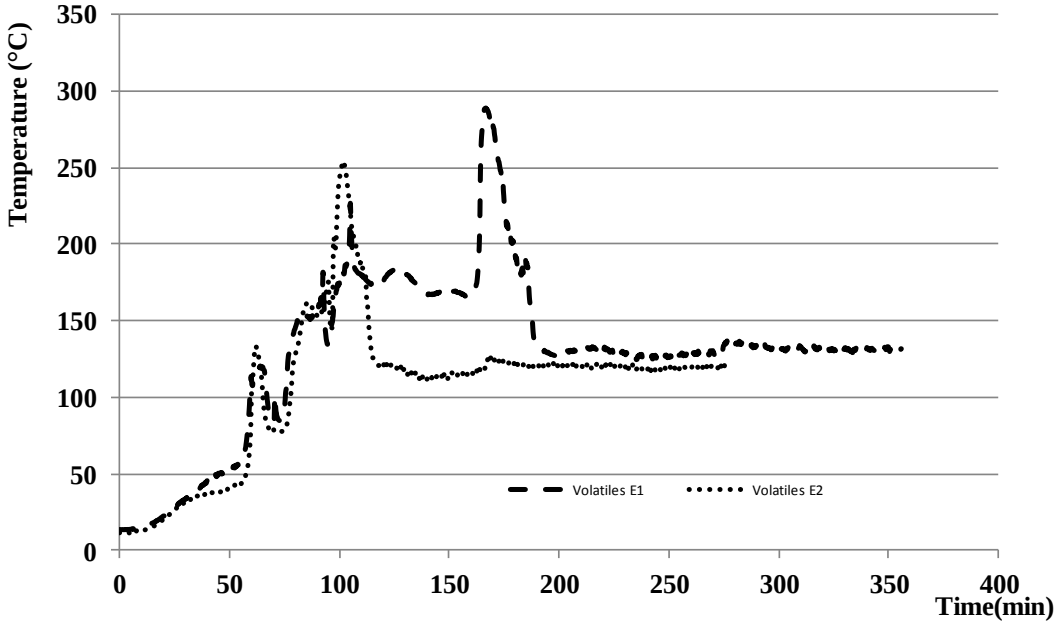


Fig 3-5, Temperatures of Volatiles E1 and E2.

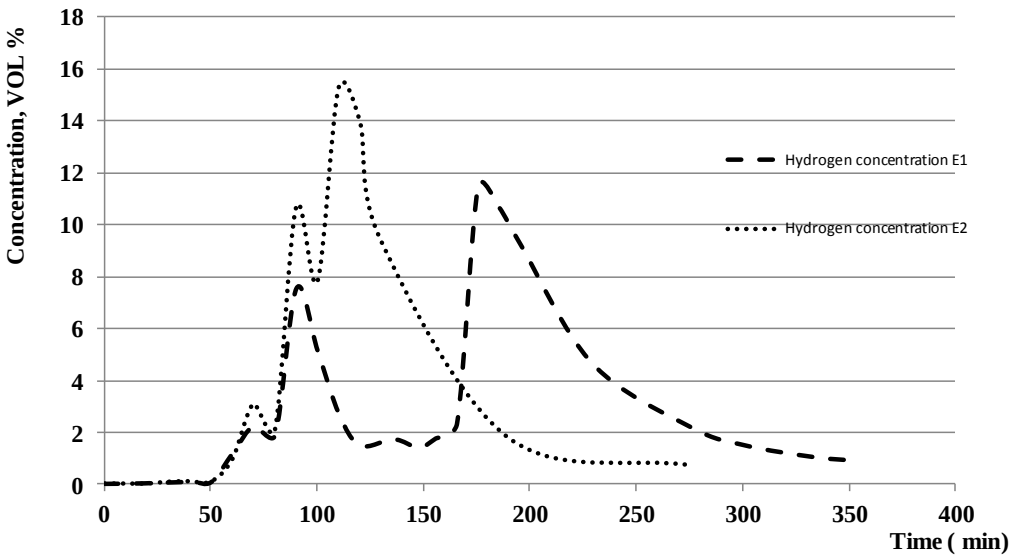


Fig 3-6, Hydrogen concentration Vol%, E1 and E2.

2- The pyrolysis process finishes after ≈ 30 minutes of reaching 500°C. This could be emphasized by elementary analysis of remained char in the reactor and calculated the percentage of hydrogen residue in it. The pyrolysis finishes when there is no more hydrogen in the char [ref 12in chapter 1]. Table 3-3 shows the H concentration in the char residue and the efficiency of pyrolysis (process completion) for both programs.

Characteristics	E1	E2
H %	0.69 ± 0.40	0.48 ±0.07
Solid yield %	40.82 ± 1.19	39.97 ± 0.66
Pyrolysis efficiency	95.92	97.22

Table 3-3. pyrolysis efficiency. E1 and E2.

Pyrolysis efficiency is calculated via the following equation 3-1

$$pyrolysis\ \ efficiency\ \% = 100 - \frac{Y \times H_{solid}}{H_{scrap}} \qquad 3-1$$

Where Y is the solid yield. H_{solid} is the concentration of H in char residue and H_{scrap} = 6.9 is the H concentration in the tire before pyrolysis (table 2-1).

Little bit higher efficiency with E2, this could be explained by the 400°C isothermal heating time (80 min) which gives more time of contact between the vapor and the char to take place. This provokes the carbonaceous reaction to happen again. The produced molecules deposit in the char pores and stay there. It is difficult to go out else at high temperatures (over 800°C) [3,4].

3- The first peak, in the volatiles' curves in both programs, appears at around 250°C. This peak- depending upon the DTG results and the literatures survey [2,3,4]- related to the decomposition of additives as plasticizers and softeners. It is small enough according to the small mass percentage of theses additives (max 9%). While the next considerable peak appears after about 65 minutes from the beginning of the process. Where the reactor temperature is actually around 380°C. 380°C is T_{max} of actual pyrolysis of rubber as have been showed in chapter 2 and which agrees with references [2,3,4 and Chapter2]. While the followed peak doesn't respect the DTG results (460°C-470°C) and it is shifted

little bit higher to around 500°C. This may due to the delay in the going out of volatiles after pyrolysis of considerable amount of tire and the empty volume in the reactor became bigger or because of the heating speed which is faster than the speed of going out of volatiles. In this case, it is possible to heat more rapidly to 350°C in order to save time.

3-II.2.1.2 Products' Yields

The products' yields for both programs are showed in table 3-4:

E1					**E2**		
Solid	Liquid			Gas	Solid	Liquid	Gas
	F1 (400°C)	F2 (500°C)	Total				
%	%	%	%	%	%	%	%
40.82 ± 1.19	24.50 ± 1.24	17.06 ± 1.00	42.46 ± 1.27	16.29 ± 1.98	39.97 ± 0.66	42.76 ± 0.84	17.18 ± 0.84

Table 3-4. Products' yields of both programs E1 and E2.

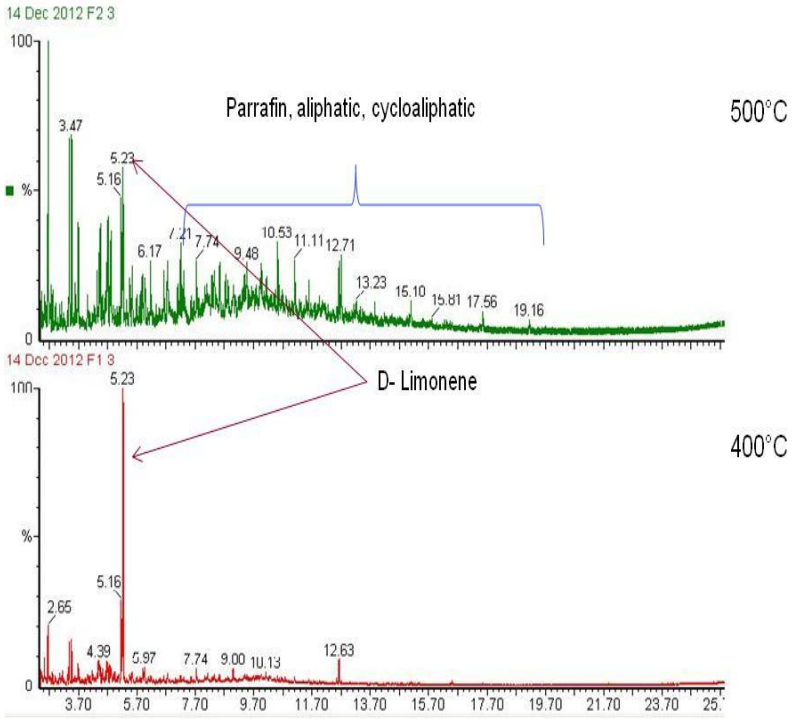
It is clear that there is no big difference from the yield point of view. It rests to investigate if there is any intrinsic difference between the two individual fractions obtained in E1 from one side, and between them and the product obtained in E2, from other side. This distinguish could be done by GCMS analysis.

It is clear from chromatogram 3-1 that the main product produced at 400°C is the limonene (5.22 min), benzene derivatives and very small amount of other aliphatic/aromatic compounds. While rising up to 500°C, a very wide and complicated range of aliphatic/aromatic compounds are produced.

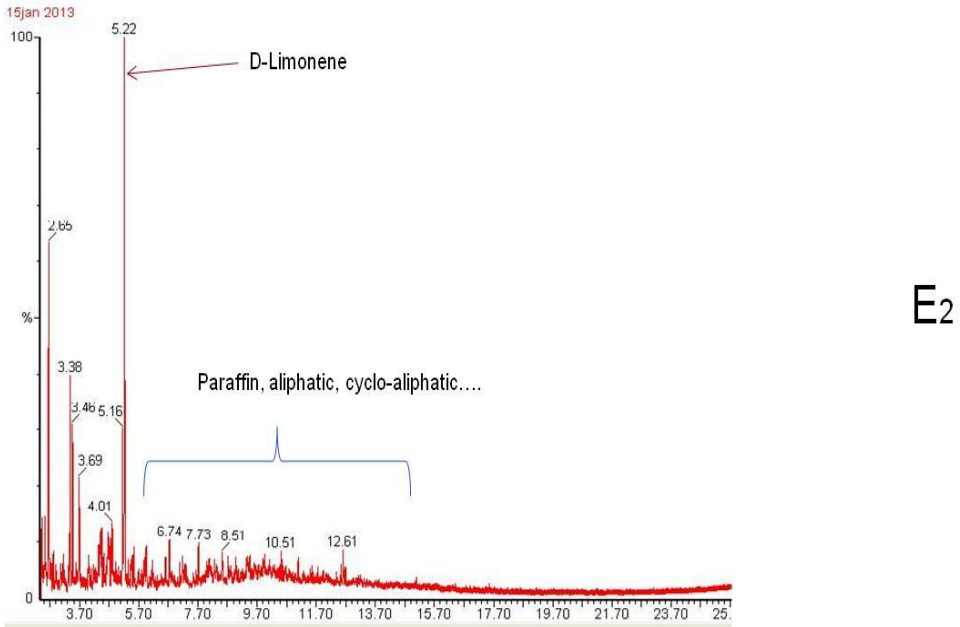
In the chromatogram 3-2. D-limonene is the dominant compound with more aliphatic compounds and single ring aromatic at the expenses of PAHs. This is desirable in fuel composition.

D-limonene is a favorable product because of its wide important uses as a feedstock in many industries [5,6]. But here, the work is interested in fuel

production more than a feedstock compounds. Production of d-limonene all over the pyrolysis process indicates that dehydrogenation /cyclisation/ aromatization reactions always takes place during the pyrolysis as D-limonene is produced via these reaction by Diels-Alder mechanism [7].



Chromatogram 3-1, GCMS analysis of two liquid fractions produced from E1



Chromatogram 3-2, GCMS analysis of liquid produced from E2

3-II.2.1.3 Conclusion

As the objective of this work is the fuel production and as the time consumption (energy as well) is very important factor in any industrial process. Continuous heating program E2 is more favorable to be followed after modifying of recommended conditions of heating rapidly into 350°C in order to save time and make better adjustment at 500°C.

3-III Step 2- stirring effect on heat homogeneity and pyrolysis process

As it has been mentioned before, the second challenge that could be studied before starting the optimization of pyrolysis experimental conditions is the effect of heat transfer in the reactor and within the tire rubber. The efficiency of heat transfer to and within the rubber affects dramatically the pyrolytic products' yields and their properties [3,4]. A stirrer has been added into the reactor in order to homogeny the temperature inside the reactor from one side and to scratching or honing the superficial layer of the pyrolysable part of tire removing it away allowing the heat to transfer easily and rapidly into the interior ones, from other side; increasing the contact surface area. In this case the reaction rate will be increased as the main reactions happen at the contact surface area.

Taking into account the recommended modifications in the previous paragraph, thermal program becomes as follow (table 3-5): heating from room temperature to 350°C with heating rate 20°C/min. Then, heating continues to 450°C with heating rate 5°C/min, after that heating becomes 2°C/min up to 490°C where the temperature is kept constant for 100 minutes. Flow rate of nitrogen is always equal to 100mL/min during the whole process duration. Another modification has been made that the sample weight has been increased from 200g in the preliminary experiments into around 700g -800g.

The mechanical mixer (photo 3-1) has three blades at the end of the axe with mixing rate of 60 rpm; it is located at the bottom level inside the reactor. It was selected with this type in order to rise up the rubber mass from the bottom into the upper level. As the rubber is pyrolysed gradually from the outer layer into the

interior. The pyrolysed part converted into fine powder and precipitates in the bottom of reactor holding part of non-pyrolysable tire. In this case, produced char prevents the heat transfer homogeneity.

Initial temperature (°C)	**Final temperature** (°C)	**Heating rate** (°C/min)	**Residence time** (min)
Ambient 15- 20	350	20	≈ 17
350	450	5	20
450	490	2	20
490	490	-	100
Time up to 500°C ≈ 160 min			

Table 3-5. Thermal program with/out mixer.

Photo 3-1. The mechanical mixer added to reactor

Each experiment will be repeated three times at least.

3-III.1 Results and discussion

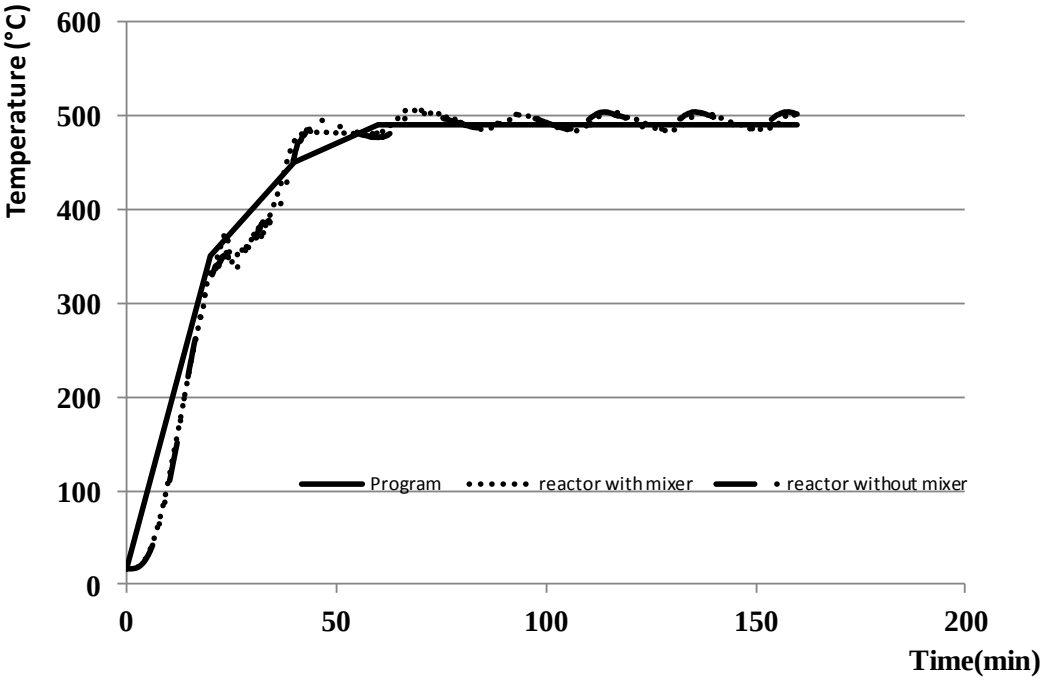


Figure 3-7, reactor temperature behavior of two cases with/out mixer.

First of all, the reactor temperature behavior in both cases will be shown in figure 3-7 and that of volatiles in figure 3-8.

It is clear from both figures 3-7 and 3-8 that the temperatures' curves of both cases; either for the reactor or volatiles; have the same. Little shift (delay) between volatiles' temperature after 30 minutes can be noticed when the temperature just exceeds 360°C; The temperature at which the tire pyrolysis starts (cf. DTG results, Chapter 2). In addition, volatiles' temperatures reach nearly the same temperatures. This means that; more probably; the same kind of volatiles (and not necessary the same quantity of each volatile) are produced. It means that the same thermal process takes place (Fig 3-8).

To be sure about the last conclusions, other characteristics should be examined as products' yields, gas product analysis, liquid product characterization following EN590 (density, Viscosity, flash point, Great Calorific Value GCV and distillation at 360°C) and solid product characterization (GCV and elementary analysis).

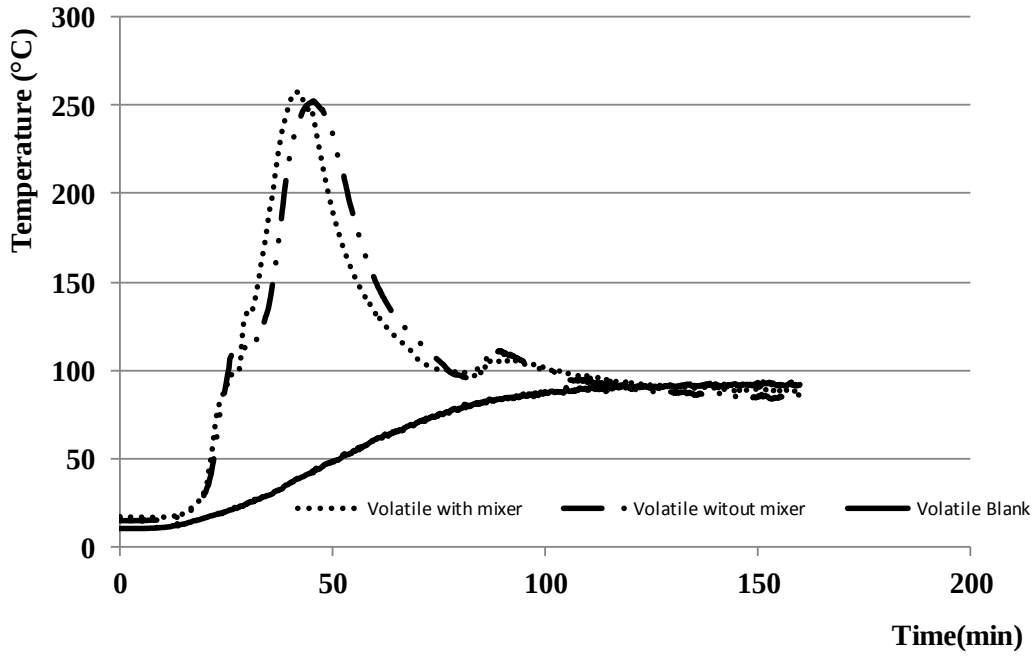


Figure 3-8, Volatiles temperature behavior of two cases with/out mixer.

3-III.1.1 Products' yields

Products' yields of the two cases with/without mixer are showed in table 3-6. Apparently, there is no difference between the two cases with/without mixer as the products' yields show no big differences between the two cases. So the question is: does the mixing effect appear in the physico-chemical properties of products? To answer this question, characterization of each product individually should be done.

Moreover, it is noteworthy that the liquid yield in both cases with/without mixing is increased slightly at the expenses of gases when sample weight is increased to around 700-800g in comparison with those of 200g (cf. paragraph 3.2) in the same reactor volume. This is due to that the empty volume; over the degradable materials inside the reactor; becomes smaller and full with bigger amount of produced vapor. In this case; produced volatiles will push its selves out of the reactor quickly preventing secondary cracking to take place; which reflect in less light volatiles.

Product Pyrolysis	Solid	Liquid	Gas	Remarks
With Mixer	38.82 ± 1.26	48.88 ± 1.13	12.30 ± 1.66	There is no significant difference between the both experiments depending upon the yields
Without mixer	39.45 ± 1.06	49.26 ± 0.61	11.24 ± 1.24	

Table 3-6. Products' yields of pyrolysis with/out mixer.

3-III.1.2 Gas Product Characterization

The main produced gases are: H_2, CH_4, CO, CO_2, C_2H_2, C_2H_6, C_3H_8 and C_4H_{10}. The more important gases are H_2 and CH_4 and they are produced in big quantities relatively to the other gases' quantities. The concentrations of all gases have the same trend (increase or decrease) during the pyrolysis. And they, as well, agree with the behavior of volatiles temperature. This means that all gases are produced in parallel at the same times from complicated reactions which happen during the pyrolysis.

H_2 concentration behavior will be taken as a representative for gases behavior and will be compared with its counterpart from another case.

H_2 concentration reaches higher value (>25 vol %) with mixing than the value (21 vol%) without mixing (figure 3-9). It means that the dehydration reaction in the presence of mixer is more severe than without mixing. Especially, C-H bond is the weakest bond in the rubber structure (Table 2-12).

An explanation to this phenomenon is that the reaction takes place at the outer layer of tire pieces more rapidly and easily than in the inner layer. In fact, the external layer is directly in touch with heat while internal layer has a delayed to be heated up to the requested temperature. In addition, the produced char; from the pyrolysis of external layer; deposits on the rubber piece isolating the rubber piece.

When mixing, it scratches the produces char layer allowing the temperature to reach rapidly into inside.

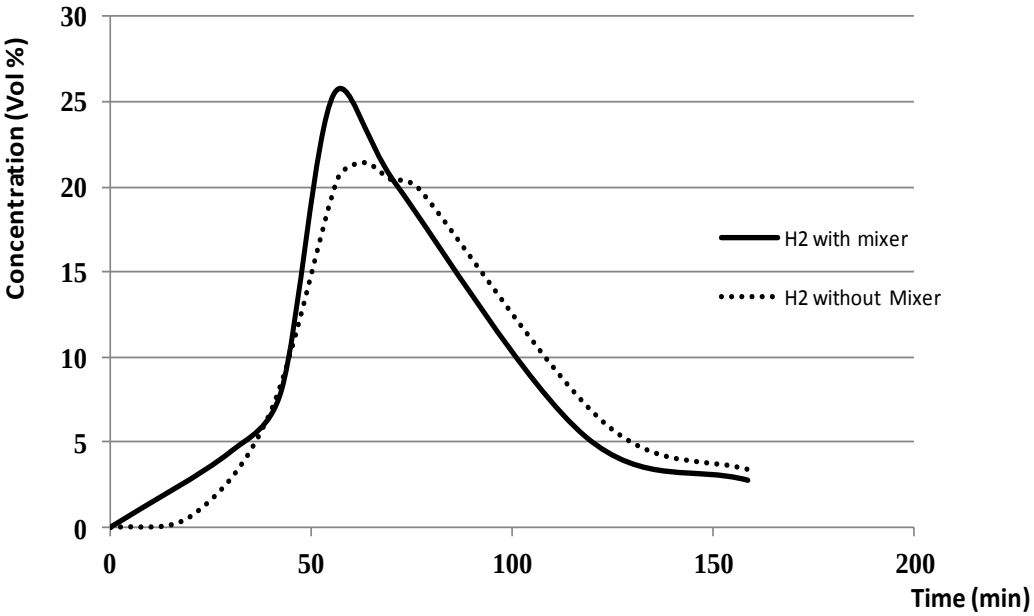


Figure 3-9, H_2 concentration in with/without mixer

Indeed, mixer makes the tire pieces turn in the reactor from edge to the center and vice versa. Temperature beside the reactor wall is assumed to be higher than in the center. In the mixer case, all the tire pieces are exposed to the same temperature in the same time. In contrary, without mixer, pieces beside the walls are exposed to higher temperature and for longer period of time comparing with those in the center which need longer time to reach the requested temperature to be decomposed. This could be proven by delay in the hydrogen concentration rising up in figure 3-9. Thus, mixing provokes severe decomposition accompanying with dehydrogenation reaction.

From other side, severe decomposition produces higher quantity of vapor; this vapor will push itself quickly outside the hot zone of reactor carrying some very heavy molecules preventing them secondary cracking reaction. This will be studied in more details in the liquid product characterization. The same phenomena could be regarded for CH_4 (figure 3-10).

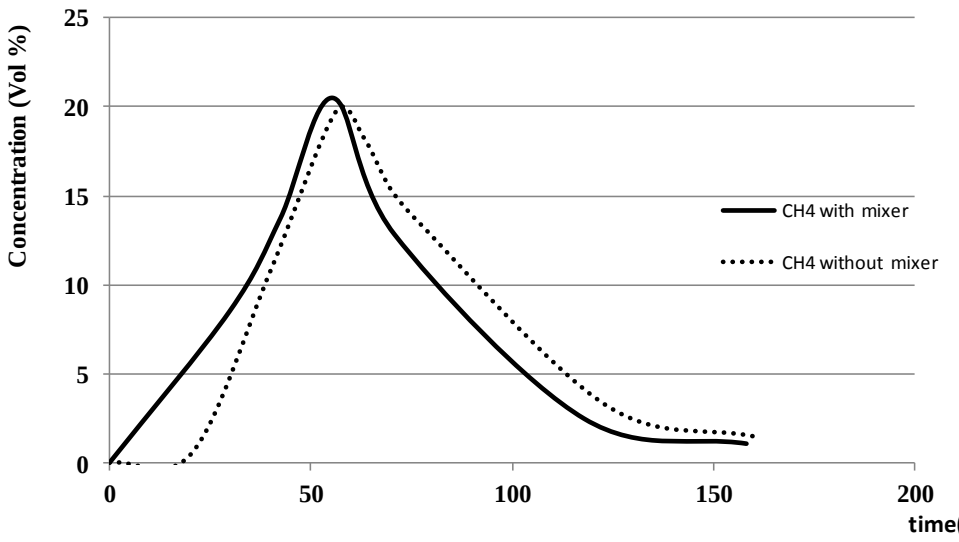


Figure 3-10, CH_4 concentration in with/without mixer

3-III.1.3 Solid product characterization

Solid product isn't very interested in this work, but its characterization gives some information about the pyrolysis process. Only two main characterizations have been examined; which are elementary analysis and GCV. The results are shown in table 3-7

Pyrolysis Condition	**C** %	**H** %	**N** %	**S** %	**GCV** MJ/kg
With mixer	71.45 ± 2.34	1.96 ± 0.33	0.36 ± 0.002	nd*	26.49 ± 0.43
Without mixer	74.53 ± 4.07	1.76 ± 0.44	0.33 ± 0.002	nd*	26.49 ± 0.08

Table 3-7. Solid products characterization. with/without mixer.* nd = non detected.

Both chars (solid products) are approximately the same. Thus, solid characterization doesn't give any new information about the mixing effect on the pyrolysis.

3-III.1.4 Liquid Product Characterization

As the liquid product is the objective of this work in order to use it as alternative fuel (diesel) in the internal combustion engine. Liquid characterization could be done following the EN590. EN590 implies more than 17 tests. It is very hard task to do all of them in each product characterization. It is time consuming and expensive. The most important and inevitable tests have been chosen to do which are:

I. Viscosity: important for the flow of fuel through the pipelines, valves and pumps. And also, fuel atomization in engine and spray burners [2].
II. Density: important for flowing as well [2].
III. Flash point: it represents the temperature that flammable gases are produced and will ignite indicating the fire hazardous associated with storage, transport and use of fuel [2].
IV. GCV: energetic and performance indicator.
V. Distillation at 360°C: content of heavy molecules (tar) [1].
VI. GC/MC: knowing the chemical composition of product which helps to have an idea about its performance inside the engine and its emission after combustion. In addition it gives good idea about its best use as fuel or feedstock. Commercial diesel available in the market has been used as reference. Results are shown in table 3-8

Pyrolysis Condition	**Viscosity** (mm^2/s. @40°C)	**Density** (g/mL)	**Flash point** (°C)	**GCV** (MJ/kg)
With mixing	4.65 ± 0.05	0.91 ± 0.01	Less than 11	42.57 ± 0.40
Without mixing	4.95 ± 1.60	0.91 ± 0.01	Less than 11	42.12 ± 0.40
Commercial diesel	3.00 ± 0.15	0.82 ± 0.05	> 60	45.90 ± 0.25
EN590	2.3-4.5	0.82-0.85	Min 60	-

Table 3-8. Liquid products characterization. with and without mixer.

There is no significant difference between the both products. But they are dramatically different from the examined diesel which respects EN590. Higher viscosity and density indicate that there are considerable amount of heavy molecules (tar). Low flash point is an evidence of the presence of very light molecules in the liquid product of the pyrolysis. But, their content in each product could be defined after distillation.

Distillation has been made in fractional distillation system with column long 40cm under atmospheric pressure. Three distinguished fractions have been obtained. The first fraction (F1) represents the light compounds with boiling point less than 110°C. Second fraction (F2) contains compounds with boiling point range from 140°C to 360°C. In this fraction compounds with boiling point around 170°C has been distilled in good amount (visional watching). This compound could be D-limonene [3,7]. The third fraction (F3) is the remained residue in the distillation flask with boiling point higher than 360°C; it is tar fraction. There was no noticeable distillation between 110°C and 140°C. Results are shown in table 3-9.

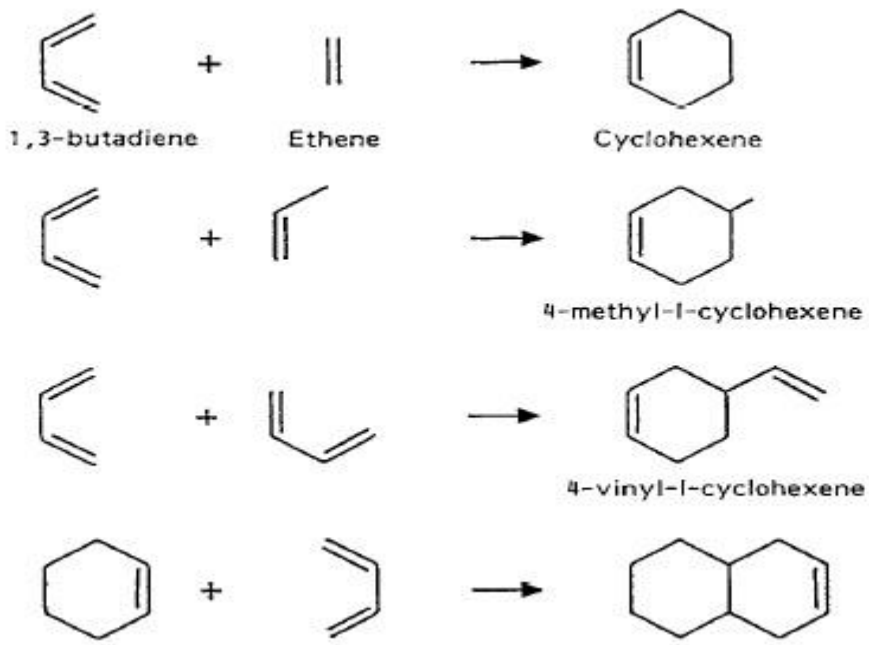
Pyrolysis/ Fraction	F1(< 110 °C) %	F2(140°C-360°C) %	F3(tar>360°C) %
With mixing	19.68	25.33	54.99
Without mixing	28.95	23.49	47.56

Table 3-9. Fractions of liquid distillation.

Both products are far from the standard EN590 which demands less than of 5% of the residue remains at 360°C. But, it is noteworthy that mixing accelerates the degradation. In this case (with mixing), and as aforementioned in gas product characterization in paragraph 3-III.1.2. Mixing allows the production of huge amount of volatile in the reactor hot zone because it increases the reaction surface and temperature homogeneity. Thermal energy will be absorbed by all rubber layers easily and quickly. In this case, volatiles push its selves quickly out of reactor preventing secondary cracking to happen. Exiting the volatile quickly causes

carrying some heavy molecules with them. This phenomena increase the percentage of tar at the expenses of the lighter compounds.

In addition, severe decomposition will provokes the concerted reaction dehydrogenation/cyclisation/ aromatization reaction via Diels-Alder reaction producing heavy molecules as shown in schematic 3-1[8].



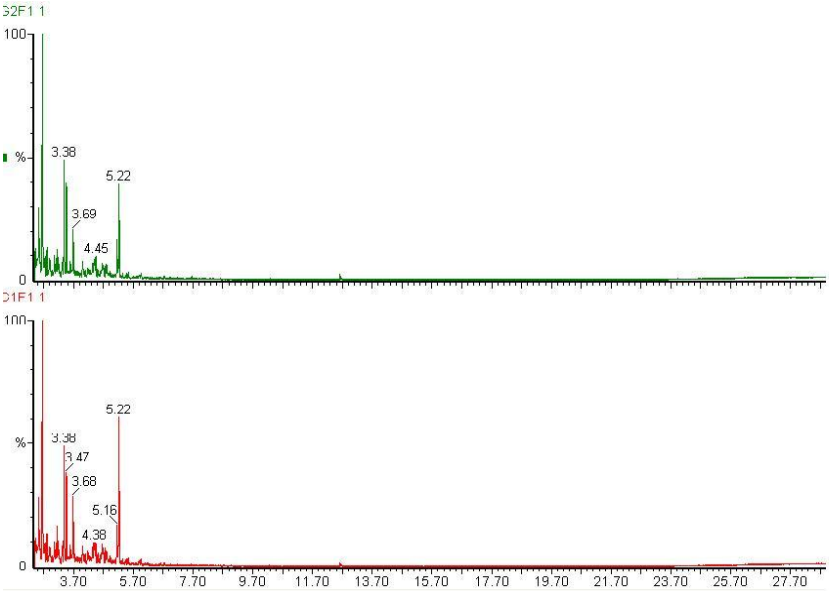
Schema 3-1, Diels-Alder aromitization [8].

Additionally, at temperature up to 300°C. tire turns into gel state. It means that its heat conductivity is improved and doesn't prevent its transition into inner layers [3,4].

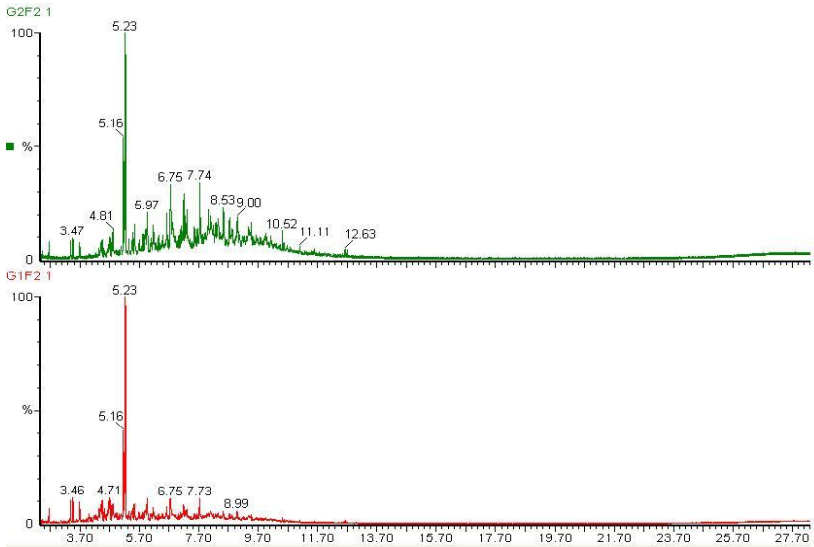
F1 and F2 are desired fractions which could be used either as alternative fuel or feedstock. As our objective is the production of fuel, GCMS analysis for both fractions in the both cases are made in order to have an idea about their composition and which one is the most suitable to be used as fuel. Results in chromatograms 3-3 and 3-4 show the available compound in the fractions of both cases with/without mixing. While chromatogram 3-5 shows the chemical

composition of diesel. G1F1. G2F1. G1F2 and G2F2 are F1 with mixing, F1 without mixing, F2 with mixing and F2 without mixing respectively.

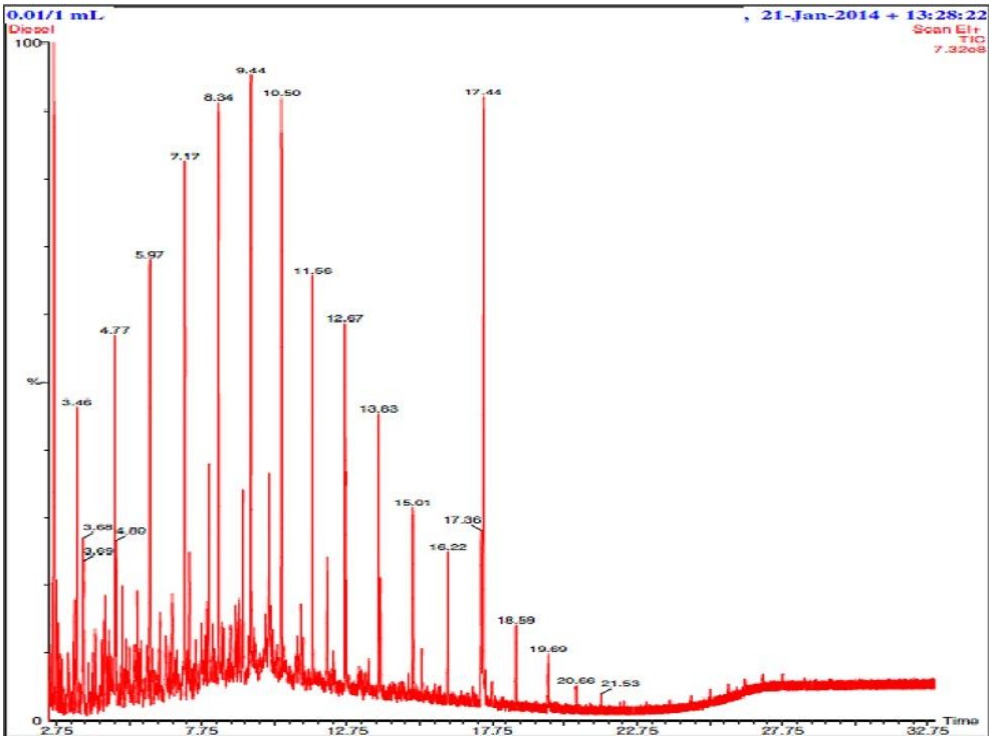
It is clear from chromatograms 3-3. F1 of both liquids are the same that they contain Ethylbenzene (3.38), P-xylene (3.47), Nonan (3.68) benzene (1-methylethyl) (4.38) and D-limonene. All of these compounds are valuable in industries or other applications.



Chromatogram 3-3. F1 chemical composition of both with/without mixing



Chromatogram 3-4. F2 chemical composition of both with/without mixing



Chromatogram 3-5. Diesel chemical composition.

F2, which is considered as the fuel fraction, is far from the diesel (chromatogram 3-5) and it is different from each other in both liquids (chromatograms 3-3 and 3-4). The main compound is d-limonene. D-limonene is valuable product and it can't be avoided in scrap tire pyrolysis but it is not the objective of the work.

F2 in the product obtained without mixing contains more aliphatic and aromatic compounds, which are intrinsic in fuel composition, than this produced from using of mixing.

3-III.2 Conclusion

Mixing has negative consequence on the quality of liquid product. It increases the degradation rate by increasing the contact surface increasing the tar content in the liquid. Tar content is increased in two simultaneous processes:

A. Exposing tire to severe decomposition provokes simultaneous reactions dehydrogenation/ cyclisation/ aromatization process.

B. Production huge amount of volatile at the hot zone of reactor. this volatiles go out of the reactor quickly carrying some heavy molecules and minimizing their secondary cracking.

Thus, next step of work will be the optimization of pyrolysis parameters temperature, Heating rate and inert gas flow rate without mixer.

3-IV Optimization of pyrolysis parameters

Parameters optimization is now the key step in the scrap tire pyrolysis. The parameters to be optimized are Temperature (T), Heating Rate (HR) and inert gas Flow Rate (FR). As the number of parameters to be optimized are three. The best way of optimization is by applying Factorial Fractional Design (FFD). FFD consists of study the factors at two levels; lower level and upper level; and find the interaction between them [9, 10, 11, 12]. This demands limited number of experiments related to the factors number and their levels. It is expressed by equation 3-2

$$\text{Experiment number} = Y^x \qquad \text{eq 3-2}$$

Where Y is the level's number and x is the number of factors. Applying this to our case leads to $2^3 = 8$ experiment. Each experiment will repeated three times at least.

The levels' values are shown in table 3-10

Factor	Lower level	upper level
HR °C/min	1	5
FR mL/min	0	100
T °C	435	500

Table 3-10. Factor levels for FFD.

Levels' selection depended mainly on DTG results. There was no big difference between 5°C/min and 9°C/min. but the difference was essentially between 5°C and 9 °C/min from one side and 1°C/min from other side. This was the criterion for 1°C/min and 5°C/min selection.

Highest needed temperature to complete the pyrolysis was 500°C. While the lowest end of degradation zone was at ≈440°C with HR=1 [table 2-9]. Taking into account that T exceeds the limiting value (because of controller fluctuation). It means that there is no sense of increasing the temperature upper 500°C and the pyrolysis doesn't finish or consumes very long time under 435°C. These are the reason for chosen the values of lower and upper levels of temperature.

DTG/TGA study showed that FR has no significant effect on the yield of pyrolytic products. This means that there is no necessary to insert nitrogen gas inside the system from economic point of view. In addition, produced gas will contain considerable amount of inert gas reducing its volumetric calorific value. This means, it is enough to purge the system with inert gas. Then stop it once the pyrolysis process starts. The produced volatiles will push themselves to go out the reactor. Then, FR=0 has been chosen to be the lower level.

But; theoretically; inert gas plays intrinsic role carrying out the volatiles out of reactor reducing the secondary cracking reaction. As the previous experiments have been made under 100 ml/min of nitrogen; which is very common value in the literature survey; this will be kept as upper level.

FFD will be applied on two objects, liquid product yield as it is the objective of this work and its quality (tar content). As it is aforementioned, tar content is the paramount test to judge the quality of the liquid product .

Lower level of each factor will be signed by (-) and upper level will be signed by (+). The effect of each factor individually or its interaction with other factors calculated via Yates's algorithm method [9,13]. Results are shown in tables 3-11 and 3-13 and in figures 3-11 and 3-12.

3-IV.1 FFD on liquid products

Yates's algorithm application is showed in table 3-11 and figure 3-11.

Experiment	HR	T	FR	Liquid yield %	factors' effect
1	-	-	-	36.26	40.905
2	+	-	-	38.19	0.695
3	-	+	-	37.06	0.825
4	+	+	-	41.46	1.425
5	-	-	+	45.36	2.6625
6	+	-	+	40.51	-0.8875
7	-	+	+	42.16	-0.1925
8	+	+	+	46.24	0.8075

Table 3-11. FFD of HR, T and FR on liquid yield.

It is clear from table 3-11 that the lowest liquid yield is when all factors are at the lower levels. Conversely, the highest is when they are at the upper ones. This means that actually all of them affect the yield.

From one side, fig 3-11 shows that the positive effect on liquid yield happens in two situations. Either both T and HR are at upper levels. Or the FR is at its higher level. Because, only in these both situations the effect is bigger than the standard bar. While in all other 7 situations, the effect is either non significant or negative. This disagrees with DTG/TGA results in chapter 2 for the reasons mentioned there (direction of the flow rate and configuration of the instrument) and agree with the hypothesis saying that inert gas helps carrying out the volatiles out of reactor preventing secondary cracking which convert part of condensable volatiles into gases.

The question which could be raised up is: does the increase in the liquid yield using inert carrier gas is at the expenses of tar content? Because it carries very heavy molecules! To answer this question, FFD will be applied on tar content in the liquid yield of the same experiments used in liquid yield effect.

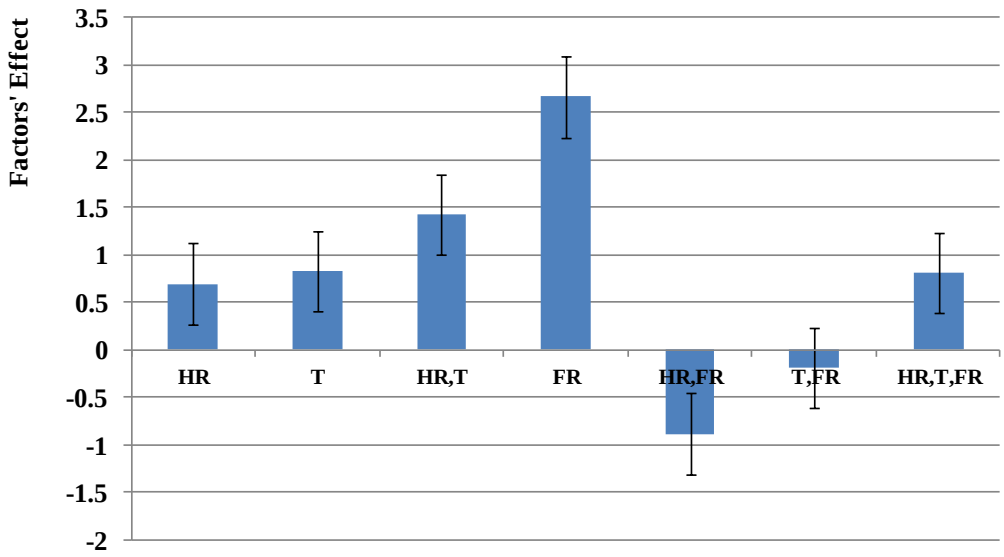


Figure 3-11, FFD for yield of liquid product. Temperature, Heating Rate and Flow Rate effect

Then, to obtain a good liquid product yield this demands working under one of two opposite situations. In these situations. Either both T and HR rate at higher from one side and FR at lower level from other side or vice-versa.

3-IV.2 FFD on tar content in liquid product

Yates's algorithm on tar content is shown in table 3-12 and figure 3-12

Experiment	HR	T	FR	Tar content %	factors' effect
	-	-	-	8.63	11.835625
HR	+	-	-	9.98	2.420625
T	-	+	-	10.34	1.163125
HR.T	+	+	-	11.86	1.748125
FR	-	-	+	11.37	1.633125
HR.FR	+	-	+	12.71	1.703125
T.FR	-	+	+	7.32	0.265625
HR.T.FR	+	+	+	22.475	1.705625

Table 3-12. FED on tar content in liquid product.

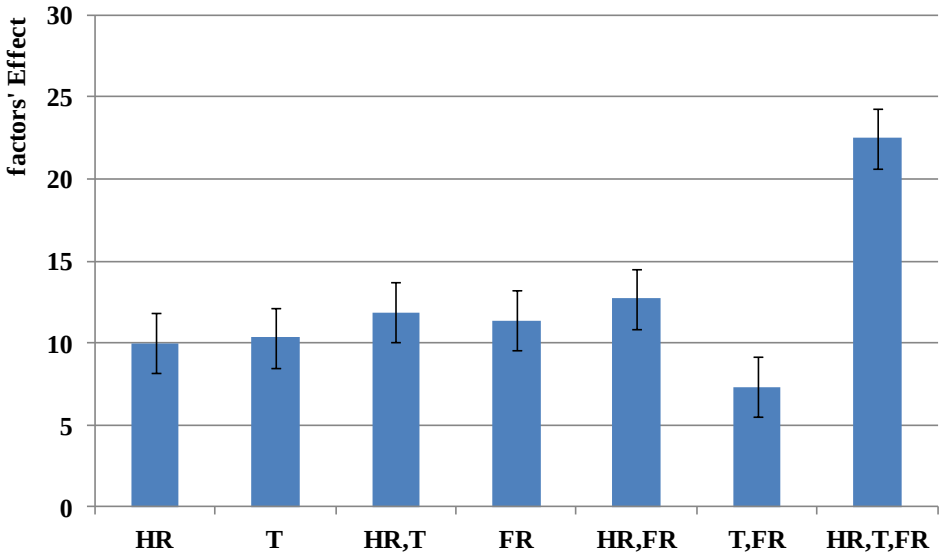


Figure 3-12, FFD for tar content in liquid product, Temperature, Heating Rate and Flow Rate effect.

Table 3-12 shows clearly that the lowest tar content; what is desired and demanded to improve the liquid quality; is when only HR is at lower level. On the other hand, its highest content is when all the factors are at their upper levels, undesirable result. This means that all factors have positive effect on tar content (negative on liquid quality). To have an idea if there is a factor that has more significant effect Yates's algorithm is used and results are shown in figure 3-12

Figure 3-12 proves that all factors, without any exception, have significant positive effects on the tar content either individually or in combined. But, the lowest effect is observed when T and FR are combined.

3-IV.3 Conclusion

HR and T are unavoidable parameters. FR gives negative effect when it interacts or combined with other factors. In addition, carrier gas reduces the volumetric calorific value of produced gas via diluting it. Thus, Pyrolysis will continue without carrier gas during the process but it will be just purged for limited time to get rid of

oxidative gases (O_2 . CO_2 and H_2O). Then it is stopped once the pyrolysis starts. And the optimization will be limited on HR and T.

3-V Optimization of temperature and heating rate

Now, and after the decision to exclusion of inert gas from the pyrolysis and limiting his role to purge the system with inert gas before the pyrolysis process preventing any oxidation process to take place. The rest two parameters T and HR will be studied individually profiting from remarks obtained in both chapter 2 and paragraph 3-IV.

In this part of work, at the beginning T will be fixed at 500°C and HR values will be changed. HR is very important to be studied precisely because it is considered the key factor to control the transfer of heat from heater (resistance) to tire. This transferred thermal energy is divided into two parts which are [4]:

1) Heating the entire system (including the tire): Rising up the temperature from room temperature to required one (500°C for example).
2) Support the reaction enthalpy: the required energy to convert the tire into the pyrolytic products.

Table 2-9 shows that the maximum required activation energy is 135 kJ/mole. It is relatively low and should be well respected. Because, if extra heat (or energy) has been introduced. It can provoke both phenomena which are: side reaction between volatiles compounds, and complicated parallel decompositions of tire. In addition, extra energy can provoke creation of free radicals; the most worse in these phenomena is the production of hydrogen molecules or hydrogen free radical. Hydrogen production (in both cases) will be at the expenses of cracking the bond C-H producing active carbon atom. This active carbon atom trends to stabilize via combination with other atom(s) from the same molecule (intramolecular reaction) or from a different one (intermolecular reaction). Then. cyclisation/aromatization/ re-polymerization processes will take place leading to undesirable PAHs or tar formation.

For that, research for best value of HR is very necessary; this is via change the power supply (puissance). Powers with 500W, 750W, 1500W and 3000W have been used for this purpose. The HR equivalent to each power is showed in table 3-13.

Power (W)	Equivalent HR (°C/min)
500	0.85
750	1.17
1500	7
3000	16

Table 3-13. Equivalent HRs of resistance puissance.

3-V.1 Results and discussion

3-V.1.1 Temperatures' behaviors (reactor and volatiles)

First of all it is better to have a look at the reactor temperature behavior related to each puissance. It is shown in figure 3-13.

With power (puissance) 500W, reactor temperature doesn't reach 400°C (387°C). It isn't enough to pyrolysis tire. This will be emphasized in both volatile temperature and liquid product yield. While with 1500W and 3000W. Temperature exceeds rapidly 500°C to 530°C and 550°C respectively. This could influence the secondary cracking of some remained volatiles in the reactor increasing the tar content as well. As high temperature promotes the aromatization reaction producing of PAHs [2,3,4]. And as a consequence, some tar quantity. This will be assured in the liquid product characterization (tar content). On the other side, with 750W temperature reaches its end (500°C) slowly and doesn't exceed it. The only disadvantage is the time consumption.

Another noticeable phenomenon is: as the pyrolysis process is endothermic at the beginning (positive Ea. Chapter 2). It adsorbs heat (energy) to take-off. This appears with power value of 500W, 750Watts and 1500 watts by sudden reduction (or change in temperature raising slope) in reactor temperature at around 300°C. This agrees with kinetic study in the Chapter 2; energetic zones (degradation) start at around 300°C.

This couldn't be seen with 3000W. It means that with 3000 W, very big quantity of energy is introduced comparing with required one. This could be reflected in complicated thermal processes (degradation. cyclization. aromatization. evaporation…etc.). But, as the C-H bond is the weakest bond in the rubber structure (table 2-11). C-H bond will be influenced remarkably leading to high H_2 production in gas product and high content of tar in liquid; will be examined in gas analysis and liquid characterization.

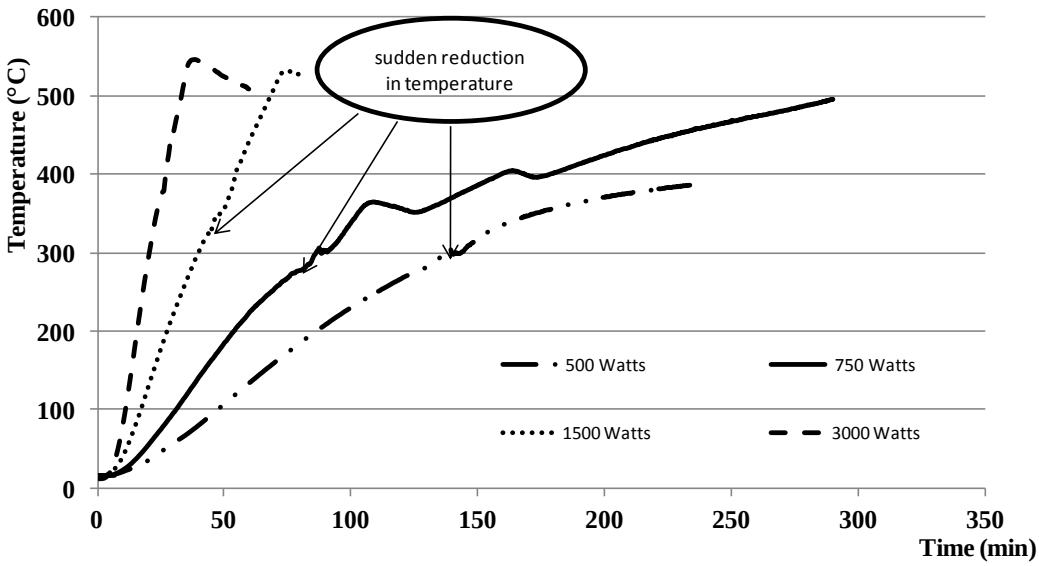


Figure 3-13, Reactor temperature behavior for different powers.

Volatiles' temperatures could give some information about the thermal phenomena in the reactor. (Figure 3-14):

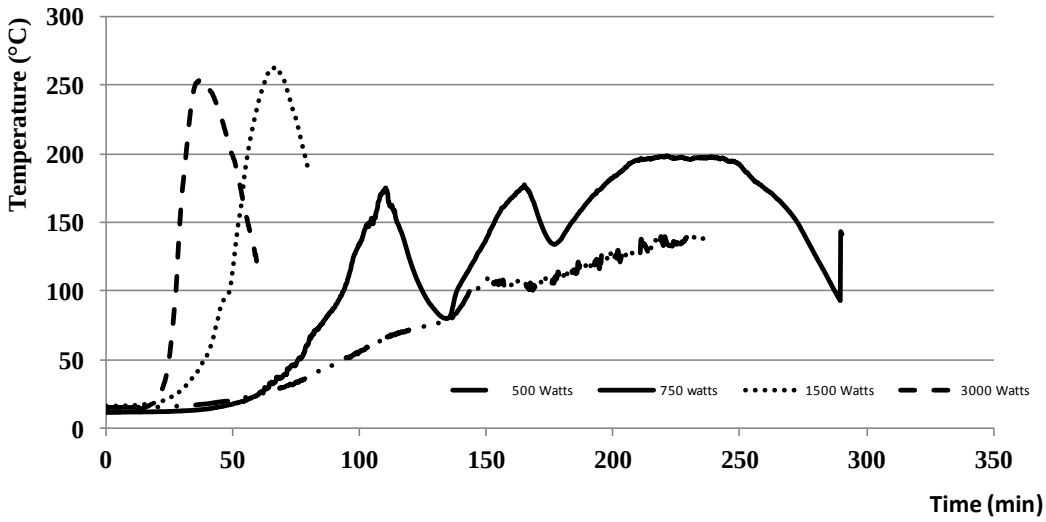


Figure 3-14, Volatiles' temperatures behavior for different powers.

Again, working with 500W isn't sufficient enough to complete the pyrolysis. Its volatiles' temperatures very low < 150°C. This means that its liquid product consists mainly of light naphtha or feedstock chemicals which aren't the present work objective.

1500W and 3000W volatiles' temperatures exceed 250°C. In addition, their temperatures' slopes are very sharp; this means that volatiles reach their boiling points rapidly making them evaporated without staying longer time for secondary cracking to lighter ones. They could, as well, carry out some heavier molecules increasing tar content in the liquid product.

750W volatiles' temperatures reach moderate value 198°C after 221 minutes of the beginning of pyrolysis. Reactor temperature at this time is around 450°C. The question is: does 450°C is sufficient to finish the pyrolysis? In this case another value about the temperature optimizing has been gotten. It will be discussed later.

Another noticeable remark with 750W is in figure 3-14. volatiles' temperatures rising (evaporation) takes place over three distinguished zones. The volatiles' T_{max} of each distinguished zone and its corresponded time and reactor temperature are shown in table 3-14:

Volatile T_{max} (°C)	t (min)	$T_{reactor}$ (°C)
174	110	364
177	164	404
198	221	446

Table 3-14. Volatiles' temperatures of 750 Watts and their corresponded time and reactor temperature.

It is agreed with DTG results in Chapter 2, that there are three distinguished zones with T_{max} values 350°C, 400°C and 445°C when HR = 1°C/min. This means that each pyrolysable part of tire takes its sufficient time to be take-off from tire into volatile phase. Then; in volatile phase; each compound faced two cases: Either conveyed directly out of the reactor, or it could be exposed to secondary cracking producing some lighter products which are favorable in liquid product. The secondary cracking always takes place in parallel with dehydrogenation process increasing gas product yield and unsaturated (aliphatic and aromatic) compound in liquid product. These unsaturated products could form the base of cyclisation / aromatization reaction via Diels-Alder reaction (schematic 3-1)

3-V.1.2 Products' yields

Products' yield are showed in table 3-15

Puissance (watts)	Solid %	Liquid %	Gas %	Volatiles (liquid and gas)
750	45.14	40.51	14.36	54.87
1500	38.62	53.49	7.89	61.38
3000	37.83	46.86	15.31	62.17

Table 3-15. Pyrolytic products' yields with different puissances.

First of all, comparing volatiles' yields (liquid and gas) from one side and solid yields from other side, both 1500W and 3000W respect the results of TGA in Chapter 2. While 750 Watts produces lower volatile yield at the expense of higher solid yield. This could be explained in one of the following reasons:

1- Using power of 750W doesn't introduce sufficient energy to decompose tire completely.
2- Tire is decomposed completely. But some produced compounds of the decomposition are very heavy with very high boiling points. 750W can't supply the sufficient heat to evaporate them completely. They re-condensed in the tube once they go out the reactor or at the inner surface of the cover of the reactor and drop again over the char. They could decomposed slightly with time or evaporate slowly as well.

In both cases, it is better to keep these heavy compounds in the solid product instead of their moving to the liquid product. Because they improve the solid energetic quality (GCV) and it is easier to extract them (treated) in the solid phase.

Liquid yield with 750W; which agrees with literature works as Aydin et al [13] 31-40% and Banar et al [14] 39% and Laresgoiti et al [15] 38%, even under different conditions of temperature and heating rate; is lower than those for 1500W and 3000W. Whatever is the volatile's distribution between gas and liquid, the question is: does this affect the liquid quality? Liquid characterizations are shown in table 3-16.

Low density and viscosity values of 750W liquid show that heavy compounds (tar) are existed in less quantity than the available one in liquids produced from both 1500W and 3000W. Distillation emphasized the same point as the tar content in 750W liquid (10%) while it is (41%) and (38%) in 1500W and 3000W respectively.

In all cases, liquids couldn't be used directly in engines or burners. They should be exposed to post-pyrolysis treatment, specially filtration and distillation in order to respect the EN590.

Liquid characterization	750 (W)	1500 (W)	3000 (W)
Density (g/ml)	0.85	0.91	0.91
viscosity @ 40 m.Pas	1.15	3.3	2.35
flash point (°C)	25	black smoke at 30°C	
GCV (Mj/kg)	43.94	43.47	43.47
S%	nd* (< 0.2)	0.91	1.05
F1. Light naphtha < 110 °C vol%	9.88	15.84	12.28
F2. Fuel [140°C - 360°C] vol%	79.78	42.97**	49.81**
tar content. F3>360°C vol%	10.34	41.19	37.91

Table 3-16. Liquid product characterization of 750, 1500 and 3000 W.*nd=non detected. 0.2% is the limit of detection of the instrument ** no visual noticeable distillation after 270°C.

Both F1 and F2 are interesting even F2 is considered more favorable than F1 as it is the objective of this work. But, as the table 3-17 shows; the final liquid yield should be recalculated taking into account the final usable product after distillation (emitting tar content); making correction into raw material. The new calculation relates to the F1and F2 individually and together. The results are showed in table 3-17.

Experiment	F1	F2	F1+F2
750W	4.45	35.90	40.35
1500W	8.55	23.20	31.75
3000W	5.77	23.41	29.18

Table 3-17. Final liquid yield recalculated relatively to raw materials.

So, pyrolysis with 750W is the better to be applied on the tire pyrolysis.

Indeed, as aforementioned, the strength of force of pushing out the reactor is decreased when the reactor temperature reaches 450°C. Back to DTG results; specifically to figure 2-14 and table 2-8; we can note the following:

In figure 2-14. T_{max} of the last (third) degradation zone is 460°C, where the maximum degradation rate takes place. The weight loss after this temperature forms ≈14% of the pyrolysable mass. This 14% could be due to either continuous tire pyrolysis or evaporation of some heavy molecules. In both cases, the majority of this part of mass is supposed to be heavy compounds as they are formed or evaporated at relative high temperature and as it has been mentioned in many literatures [3,4,16]. These compounds are undesirable in the liquid product.

Otherwise, table 2-8 indicates that the end of last energetic zone is about 475°C. It means that the degradation process is finished at this temperature. Any other thermal process above this temperature will be mostly due to evaporation. Thus, relating to the two previous points, temperature will be fixed at 465°C taking into account that temperature controller fluctuates little bit and as consequence temperature could exceed 465°C by about 10°C.

Another noteworthy characteristic is the Sulfur content; it is decreased dramatically at low resistance puissance. This could be explained that, with high puissance (power), a vigorous decomposition takes place producing free radicals of elements C, H, S. This gives the opportunity to a very complicated reaction to take place producing unexpected compounds. While with low puissance, the introduced energy is sufficient to break down some limited bonds. As a consequence, each produced free radical of H and S will form H_2 (g) and S_2 (s), or H_2S (g). As the bonds H-H, S-S and H-S are more stable than C-H and C-S depending on their dissociation energy which are H-H= 436kJ/mole. S-S = 429 kJ/mole. H-S=344 kJ/mole. C-S = 699 kJ/mole and C-H = 337 kJ/mole [32. table 4.11 therein].

3-V.2 Conclusion

Batch of energy, which the tire is exposed to, plays a very important role in tire rubber decomposition into liquid oil qualitatively and quantitatively. In our case, depending on the scrap tire raw material and the reactors configurations (height, diameters), using resistance with puissance higher than 750W leads to bad quality liquid product; in spite of higher puissance produces higher liquid/volatile yield.

A power value of 500W doesn't supply sufficient energy to increase the system temperature to the required one. As a consequence, the pyrolysis process stops at low level of decomposition.

Then, looking for the best power is intrinsic in scrap tire pyrolysis in order to supply the required energy to decompose limited kind and number of available bond C-S, S-S, C-H, C-C, C=C, preventing severe cracking which produces a huge number of free radicals. Then, as a consequence, non-controller complicated and enormous number of reactions will take place leading to unexpected results.

The next step will be investigating the best power in the range [500W - 750W] at maximum temperature 465°C.

3-V.3 Adjustment of resistance power

3-V.3.1 Temperatures' behaviors

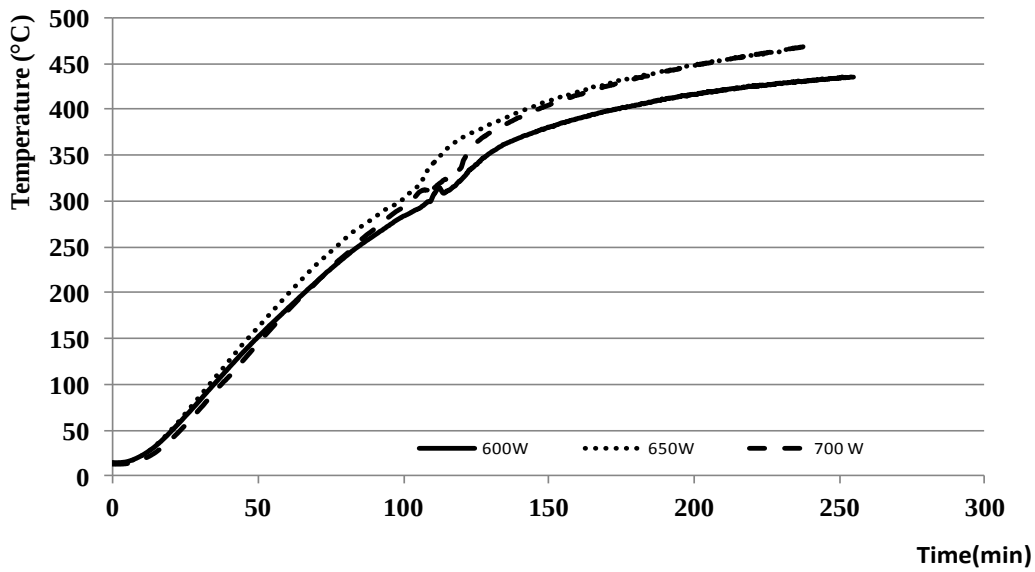


Figure 3-15, Reactor temperature behavior for different powers.

New series of power have been used; the new series' values are 600W, 650W and 700W. Firstly, Figure 3-15 shows reactor temperatures' behaviors. It is obvious that there is no big difference in tendency between reactor's temperatures curves;

especially that heating rate is close to 1°C/min for the all three curves. But the major noticeable point is that with a power of 600W temperature doesn't exceed 450°C which is not sufficient to finish the pyrolysis process completely.

Volatiles' temperatures; as aforementioned; have important sign about liquid product properties (Figure 3-16). Curve trend is nearly the same for all. But maximum temperature is dramatically different. It is 187°C for 600W while 218°C for other two power values. Indeed, volatiles' temperatures in 600W stays fixed till the end of pyrolysis time; it means that the pyrolysis didn't finished.

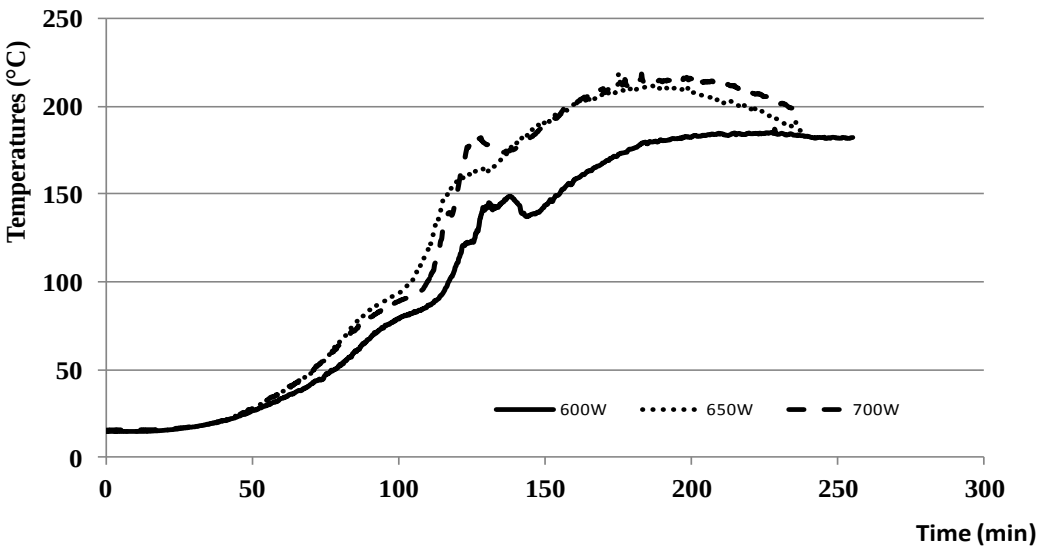


Figure 3-16, Volatiles temperature behavior for different powers.

Even the distinction between pyrolysis zones is less clear between them. This could be explained by the following: as the introduced energy is not so strong to be just enough to crack some bonds as C-S, C-H and C-C. The decomposition is so slow and the evaporation of produced volatiles is so slow as well. Thus, along the process time there are always two thermal processes: decomposition and evaporation. As a consequence, the evaporation of some compounds overlapping preventing separation between them.

The question which arises now: Does it affect the products properties? We will check this in the next paragraph?

3-V.3.2 Products' Yields

Table 3-18 shows the pyrolytic products' yields of the three values for the power.

Experiment	600W	650W	700W
Solid	46.67	45.96	44.09
Liquid	39.65	42.82	42.04
Gas	13.68	11.22	13.78

Table3-18. Pyrolytic products of 600W. 650W and 700W.

Little increase in the volatiles yield; in respect with the puissance increment; takes place. This is at the expenses of solid yield reduction. Higher solid yield with 600W emphasizes the information given by reactor and volatiles temperatures' curves that the pyrolysis wasn't finished with 600W. Or; at least; many heavy molecules couldn't be evaporated completely. But how does this reflect in the liquid characterization? Table 3-19 shows that:

Experiment		**600W**	**650W**	**700W**
GCV (KJ/kg)		43.9	45.5	43.62
F1 (%)		9.46	10.58	8.48
F2	(%)	83.19	82.27	81.75
	GCV	44.81	46.07	44.39
S%		nd (<0.2)	nd (<0.2)	nd (<0.2)
Tar (%)		7.35	7.15	9.77

Table 3-19. Liquid product characterization 600W, 650W and 700W.

Actually, 650W gives better liquid product with comparable GCV, Yield and tar content. So, working with 650W is favorable to be used in tire pyrolysis depending on the used reactor configuration.

650W is suitable to crack the specific and limited number of bonds in the rubber structure. The bond position plays very important role in the type of produced volatile compounds [17-18]. For example, Choi et al [17] showed that the decomposition at (a) position is preferable than the other two positions (b) and (c)

as shown in figure 3-17, because of stability of produced compounds due to the resonance effect. In addition, cracking at (a) position produced aliphatic derived benzene compounds with long aliphatic chain, which is more desired in fuel composition.

GC/MS characterization showed that all liquid products contain approximately the same chemical compounds of aliphatic (saturated. unsaturated and cyclic) and aromatic compounds. But they may differ in concentration which should be study quantitatively in more details.

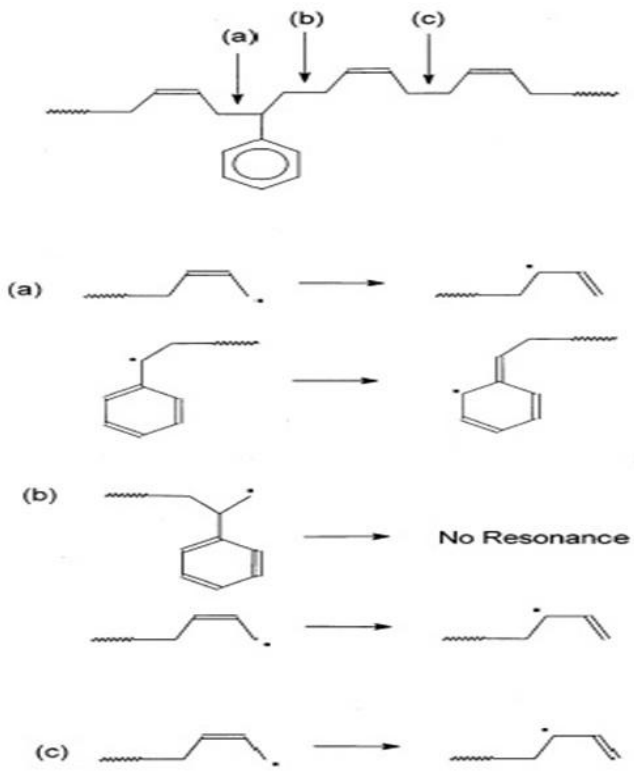


Figure 3-17, position of bond cracking [17].

Finally, comparing with literature work table 3-20, low power gives liquid product with better quality from the tar content point of view.

Reference	15	19	20	21
Tar %	30	8	25	56

Table 3-20. Tar content.

3-VI Conclusion

Three parameters have been taken to be adjusted and optimized which are temperature, heating rate and inert gas flow rate.

Inert gas flow rate affects positively the quality of liquid product by carrying out heavy molecules out of reactor into liquid product. These heavy molecules increase the tar content which is dangerous when it is inside the engine and diminishes its performance. In addition, it raises the viscosity and density of liquid product; which affect badly the liquid flowing in the pipelines system. So, pyrolysis will be without any current of inert gas and its role is limited on purging the system for 30 minutes before the pyrolysis in order to get rid of oxidative gases.

Temperature is determined precisely by the volatiles temperatures' curves in addition to the end of the last energetic zone. When volatile's temperature starts to go down towards blank one, the corresponded reactor temperature is considered the best final temperature. Heating higher this limited value add nothing to the pyrolytic product except increasing the gas yield little bit. But; on other hand; it consumes more energy and time. Thus, in this study, 465°C is the optimal temperature to work with.

Heating rate optimization shows that it only reflects the quantity of energy introduced to tire rubber to be decomposed by time unit. In other words, its role is to give indication about the temperature inside the reactor, which is not necessary to be the same as inside the rubber pieces. This means that it is better to optimize the input energy which affects the rate and type of chemical bond decomposition, determining the properties of the pyrolytic products, especially the liquid one (density, viscosity, GCV, flash point and tar content). In this study, 650W puissance is sufficient to supply the sufficient energy requested to the decomposition producing liquid product similar to the available commercial diesel.

Attention: theoretically, sufficient power could be changed depending upon reactor configuration specially its diameter. This effect is due to the heat transfer into both middle reactor and inner layers of rubber.

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Chapter 4
Engine Test

4-I Introduction

Increase in energy demand, emission norms and depletion of oil resources oriented the researchers to look for alternative fuels for internal combustion engines. Alcohols and Biodiesel; as alternate fuels; have been already commercialized in the transport sector.

This chapter presents the studies on the performance, combustion characteristics and emissions of a single cylinder four stroke air cooled DI diesel engine running with the Distilled/non-distilled Tyre Pyrolysis Oil (TPO).

First of all, depending on the result of previous chapter (3), liquid product obtained at 650W has propitious yield and competitive characteristics (GCV, S content, and tar content) in comparison with diesel (tables 3-19 and 3-20). In order to limit post treatment of liquid and maximize its usability, it was decided to compare the non-distilled liquid obtained directly after the reaction (C1) and the distilled fraction (C2) on diesel engine test bench.

Characteristics of C1, C2 and diesel fuel are shown in table 4-1.

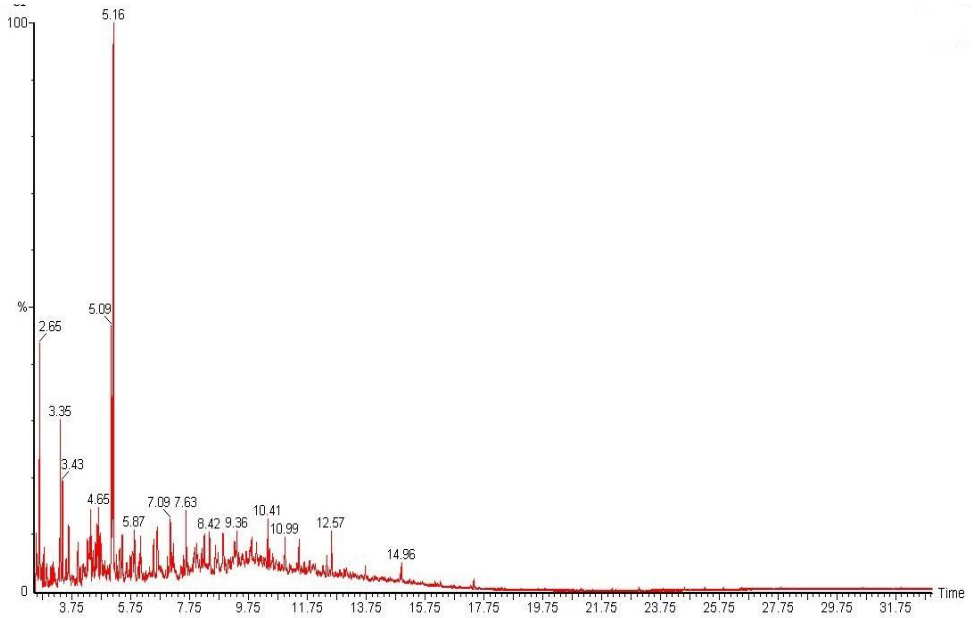
Properties/ fuel	**C1 Before distillation**	**C2 after distillation**	**diesel**
Viscosity at 40°C (mPa.S^{-1})	2.05	1.69	2.14
Density (g/ml)	0.884	0.884	0.826
Flash point (°C)	Smolder over 30°C	Smolder over 30°C	>60°C
HHV*(MJ/Kg)	45.5	46.07	45.95
LHV*(MJ/Kg)	43.6	44.2	43.1
S (%)	< 0.2**	< 0.2**	< 0.2**
C/H ration	7.9	8.0	6.3

Table 4-1, TPO and diesel properties, *HHV (High Heating Value) = (GCV) great calorific value, LHV (Low Heating Value) ** 0,2 is the instrument Limit Of Detection.

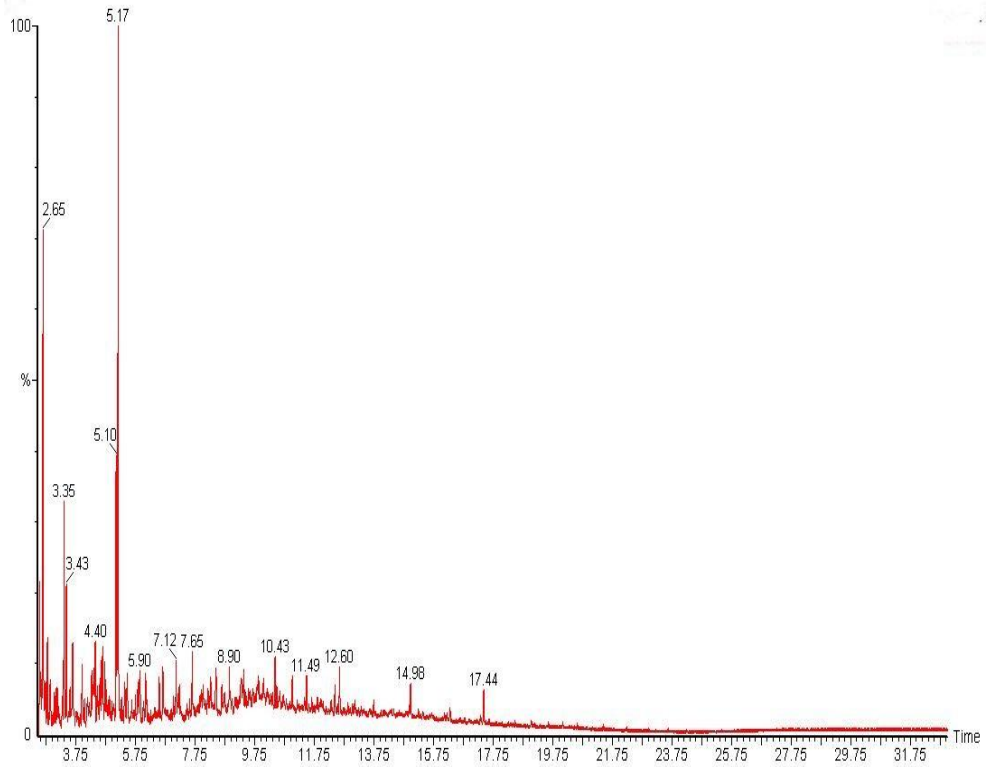
$$LHV = HHV - \frac{9\times(H\%)\times 2.570}{100}$$

It is clear that each pyrolytic liquid has higher density and C/H ratio than diesel fuel. This could be due to the higher content of PAHs which could lead to bad engine performance and emissions (THC, CO, and PM). In order to verify this

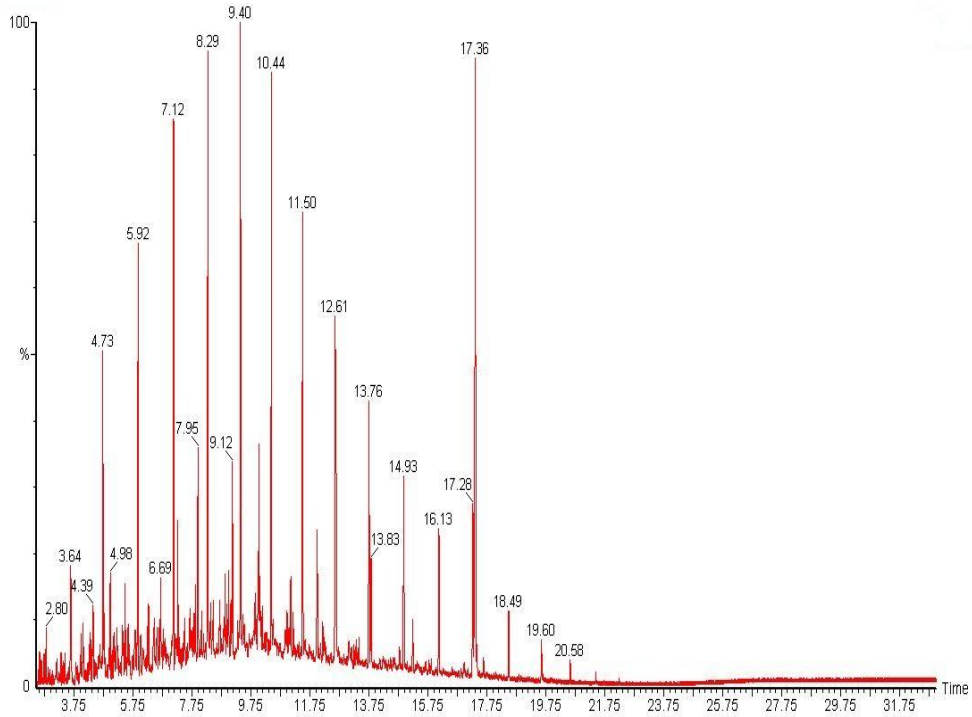
assumption, GC/MS analysis has been performed. Chromatograms 4-1, 4-2 and 4-3 show the GC/MS analysis of C1, C2 and diesel respectively.



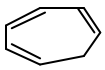
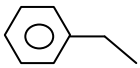
Chromatogram 4-1, GC/MS of C1

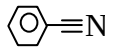
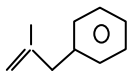
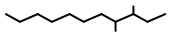
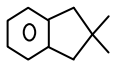
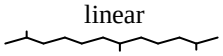
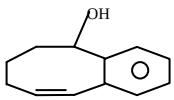
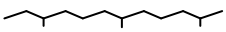


Chromatogram 4-2, GC/MS of C2.



Chromatogram 4-3, GC/MS of Diesel

RT	compound	Diesel	C1	C2	Remarks
2.69	Cycloheptatriene C_7H_8		+	+	
2.80	Octane C_8H_{18}	+			Linear
3.35	Ethylbenzene C_8H_{10}		+	+	
3.43	Benzene 1,3,dimethyl C_8H_{10}				
3.64	Nonane C_9H_{20}	+	+	+	linear
4.39	Octane,1,1-oxybis $C_{16}H_{34}O$	+	+	+	Linear C_8H_{17}-O-C_8H_{17}

4.65	Benzonitril C_7H5_N			+	
4.73	Decane $C_{10}H_{22}$	+			linear
4.98	Decane, 4-Methyl $C_{11}H_{24}$	+			Linear
5.09	1,3,8-p-menthatriene $C_{10}H_{14}$		+	+	
5.16	D-limonene $C_{10}H_{16}$		+	+	
5.87	Benzene 2-methyl-2propenyl $C_{10}H_{12}$		+	+	
5.92	Undecane $C_{11}H_{24}$	+			linear
6.69	Undecane 3,4,-dimethyl $C_{13}H_{28}$	+			linear 
7.09	1H-indene,2,3-dihydro2,2dimethyl $C_{11}H_{14}$		+	+	
7.12	Dodecane $C_{12}H_{26}$	+			linear
7.63	Bicyclonona-2,4,7-triene,7-ethyl $C_{11}H_{14}$		+	+	Complexe aromatic formula
7.95	Dodecane 2,6,11-trimethyl $C_{15}H_{32}$				linear 
8.29	Pentadecane $C_{15}H_{32}$				linear
8.42	5-benzocyclooctenol,5,6,7,8-tetra,E- $C_{12}H_{14}O$			+	
9.12	Dodecane 2,6,10-trimethyle $C_{15}H_{32}$	+			linear 

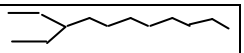
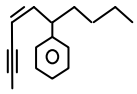
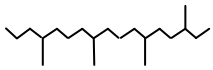
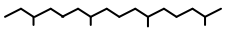
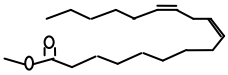
9.36	Undecane,3-ethyl $C_{13}H_{28}$			+	
9.40	Tetradecane $C_{14}H_{30}$	+			linear
10.44	Eicosane $C_{20}H_{42}$	+	+	+	linear
10.99	Z-6-phyneldec-4-EN-2-yne $C_{16}H_{20}$			+	
11.50	Hexadecane $C_{16}H_{34}$	+	+		linear
12.57	Heptadecane 2,6,10,15 tetramethyl $C_{21}H_{44}$			+	
12.61	Heptadecane $C_{17}H_{36}$	+	+		Linear
13.76	Eicosane $C_{20}H_{42}$	+	+		linear
13.83	Hexadecane 2,6,10-trimethyl $C_{20}H_{42}$	+			Linear 
14.93	Eicosane $C_{20}H_{42}$	+	+		Linear
14.96	Tetradecanenitrile $C_{14}H_{27}N$		+	+	
16.13	Eicosane $C_{20}H_{42}$	+			Linear
17.28	9,12-octadecadienoic acid(z,z)-methyl ester $C_{19}H_{34}O_2$	+			
17.36	9-octadecenoic acid methyl ester $C_{19}H_{34}O_2$	+			
17.43	Nonadecanitrile $C_{19}H_{39}N$		+		
18.49	Tetratetracontane $C_{44}H_{90}$	+			linear

Table 4-2, RT of chemical compounds in the three products C1, C2 and diesel.

Compounds' identification relating to their retention times (depending on the analysis conditions) are shown in table 4-2. It is obvious that TPO products consist mainly of variety of aromatic compounds with few aliphatic compounds (saturated

and unsaturated). In contrary, diesel contains mainly saturated aliphatic compounds (linear compounds). This emphasizes what is aforesaid that the direct use of TPO as fuel in the engine isn't possible and it accords with many literatures survey [1, 2, 3].

One of the valuable GC/MS is that there aren't sulfur's compounds detectable. It agrees with elementary analysis that the sulfur content is traceable.

To improve the quality of pyrolytic liquid to be able to use in the engine, it should be blended with commercial diesel or mixed with some additives. The best and widely applied method is the blending with commercial diesel.

Literature survey doesn't show standard or system of TPO/Diesel blending. For example, Murugan et al [1] used up to 90% and they use up to 70% in another study [4]. Martinez et al [5,6] studied the addition of 5% TPO, Ilkilic et al [7] blended up to 35%, Dogan et al [8] used 10% and Frigo et al[9] showed that blending 20% of TOP with 80% diesel could be used without any modification in the engine; while blending up to 40% TPO causes increase in CO, THC and NO_X emissions.

So, the best way to make preliminary decision about the best level of blending to be used in the engine is to measure the cetane number. For that a series of blending 25%, 50% and 100% has been applied and cetane number has been measured for all. The results are showed in table 4-3.

Liquid		**DCN**
C1	25%	44.44
	50%	32.45
	100%	16.04
C2	25%	45.25
	50%	32.37
	100%	15.46

Table 4-3, Cetane number of different TPO blending.

Cetane numbers in table 4-3 emphasize that TPO can't be used directly in the engine which leads to a consequence defective engine operation. But it has to be mixed with commercial diesel or complemented by a cetane number improver. According to the EN590 [10], the minimum cetane number is 51. But depending on

other standard or tolerance, some country in North America accept diesel with minimum value 40, and optimum range 42-45 [11]. So, as it is favorable to increase the TPO percentage in blending mixture, 25% will be accepted to do the engine test. Any increase in blending level over 25% will reduce the cetane number which reflects in bad performance in the engine [9]. In all cases, TPO couldn't replace fossil fuel totally, thus blending seems to be an effective way to valorize it in diesel engine.

Moreover, preliminary experiment has been done with 50% blending at 25% of full engine load at 1500 rpm; the knocking was perceptible during the engine running. This accords with the result of Frigo et al [9], they showed that at higher than 40% TPO, engine behavior started to be extremely irregular (i.e. power and speed unstable) with worsening in engine power output, consumption and exhaust emissions, especially at lower rpm.

A percentage of 25% of TPO before distillation (C1) with 75% commercial fossil fuel will be named C125 and C225 will be given to 25% of TPO after distillation (C2) with 75% commercial fossil fuel.

4-II Combustibles (C125 and C225) Characterization

It is important to have an idea about the properties and characteristics of new blended combustibles. The results are shown in table 4-4.

Properties/ fuel	C125	C225	diesel
Viscosity (mPa.S^{-1} @40°C)	2.00	1.88	2.14
Density (g/ml)	0.838	0.838	0.826
Flash point (°C)	45	45	>60
LHV(MJ/Kg)	40.9	40.9	43.1
S (%)	nd	nd	nd
C/H ration	6.6	6.9	6.3

Table 4-4, properties of C125, C225 and diesel.

The improvement in the properties of the blended combustibles is clear, especially either in the density and viscosity from one side, which improve the flow

in the pipelines and the atomization in the combustion chamber, or in the C/H ratio from other side, which improve the combustion process.

4-III Engine test

Engine test has been applied on engine with the following properties:

Engine: Lister Pelter TR1 type single cylinder with four strokes and air cooled. Bore 88.9 mm, stroke 95.3 mm, compression ratio 18:1 with nominal electric output at 1500 rpm is 4.5 kW.

With speed of 1500 rpm; which is normally used in production of electricity, at four levels of load which are 25%, 50%, 75% and 100% have been applied. Blended combustibles are filtered under vacuum using whatman filter paper (0.2µm) before analyzing or insert in the engine

Engine test consists of two essential parts which are:

1- Engine performance which includes the following main measurement:
   - Neat Rate of Heat Release (NRHR) and Ignition Delay (ID),
   - Brake Thermal Efficiency (BTE),
   - Brake Specific Fuel Consumption (BSFC).
2- Gaseous emissions which include the followed main emissions :
   - Total Hydrocarbon (THC),
   - Carbon Mono-Oxide CO,
   - Nitrogen Oxides NOx,
   - Particles Matter (PM).

4-III.1 Engine performance

4-III.1.1 Neat Rate of Heat Release (NRHR) and Ignition Delay (ID)

NRHR of the both blended TOP and commercial diesel at the four loading levels are shown in figure 4-1.

NRHR of different fuels were superposed at different engine loads. As it can be noticed, after the start of fuel injection (SOI), NRHR of fuel starts decreasing,

which corresponds to fuel evaporation, until reaching a minima which corresponds to the start of combustion (SOC) after which the NRHR increases sharply to form a high and narrow peak before decreasing. A second peak appears right after with smoother shape and longer duration before reaching zero level. The duration between SOI and SOC is called the ignition delay (ID), it is the duration of time where fuel starts mixing to form a combustible mixture with air and when auto-ignition conditions are reached fuel combustion occurs.

Ignition delay depends on fuel characteristics (DCN) and on combustion chamber conditions (pressure and temperature). As it can be noticed diesel fuel has a shorter ID because of its higher DCN, however, C125 and C225 have the same ID which is coherent with their identical DCN values. The first narrow peak of NRHR represents the premixed combustion phase. During the ID, a part of injected fuel is well mixed with air, and when auto-ignition conditions occur, the mixture will burn rapidly creating this sharp peak. The second peak is called diffusion combustion, it is slower than the first one because combustion occurs at the boundary of fuel jet, and mixing with air occurs simultaneously with combustion.

TPO having lower viscosity and longer ID permit a higher amount of injected fuel to be mixed with air, leading to sharper peaks and higher NRHR during premixing combustion and to lower diffusion peak because more fuel has been already burned at earlier phase. C225 has the sharper premixed combustion due to its lower viscosity and its lower heavy compounds contents.

There are obvious differences in ignition delay and in the NRHR between blended combustibles and diesel from one side, and between blended combustibles themselves from another side. Differences appear clearly at high loading levels 75% and 100%. NRHR is always the highest with C225. Differences are shown more clearly in table 4-5. As the ignition delay is due to the aromatic compounds [2], which could be the cause of low cetane number as well. In this case, it is an expected result relating to aforementioned cetane number and GC/MS analysis.

While, NRHR, which differs considerably between the three combustibles, is related with many factors which are fuel/air ratio LHV and viscosity. Fuel/ air ratio; showed in (table 4-6); especially between blended TOP combustibles, states

that there is no significant difference at all levels of loading. It means that Fuel/air ratio doesn't play any perceptible role explaining this phenomenon.

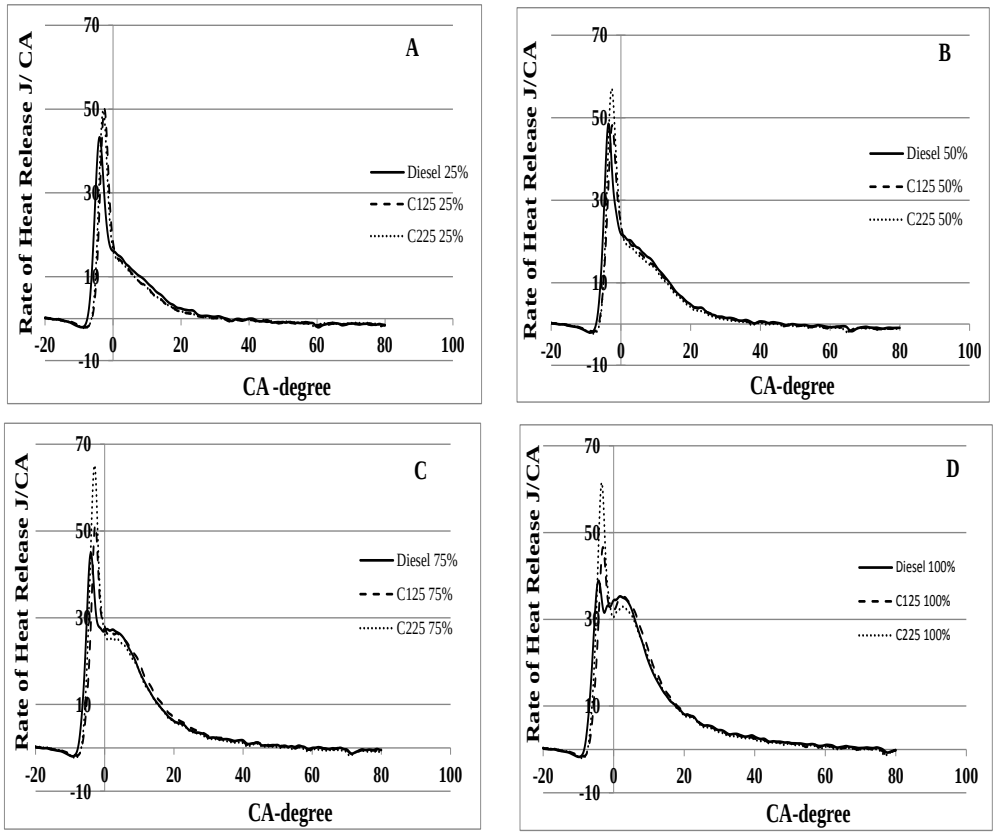


Figure 4-1, Rate of Heat Release for C125, C225 and Diesel. A= load 25%, B= load 50%, C= load 75% and D = load 100%

Combustible	Diesel				C125				C225			
Load %	25	50	75	100	25	50	75	100	25	50	75	100
Start of combustion, degree	-4	-3.6	-4	-4.2	-2.6	-2.4	-2.8	-3	-2.8	-2.6	-3	-3.2
Maximum Rate of heat release (J/°CA)	43.28	48.53	44.88	38.87	50	48.13	51.23	46.6	49.68	57.06	65.1	61.48

Table 4-5, CA of start ignition and maximum rate of heat release for the different combustibles at different loads.

Load %	Fuel/ air ratio			Equivalence ratio		
	C125	C225	diesel	C125	C225	diesel
25	0.011	0.011	0.012	0.156	0.152	0.169
50	0.017	0.017	0.017	0.236	0.231	0.241
75	0.023	0.023	0.022	0.321	0.320	0.306
100	0.030	0.030	0.031	0.426	0.425	0.434

Table4-6, fuel/air ratio and equivalence ratio for all combustibles for all load level.

Going into LHV (table 4-4), diesel should give higher NRHR, and should be no difference between blended combustibles. But it is the opposite case for C225 which gives higher values in all loading levels. In addition, the higher values for blended combustibles are with 75% loading, and with 50% for diesel. The only explanation to this behavior is that viscosity plays the intrinsic factor as the higher NRHR belongs to the lowest viscous combustible. Low viscosity helps in production good atomization, which helps to homogeneous distribution and better mixing of combustible with air inside the combustion chamber, resulting on a better combustion. While with higher viscosity, the atomization process will be poor, and vapor orients to form non-homogeneous pockets. This agrees with work of Murugan et al [2], Roche et al [5] and Martinez et al [6].

4-III.1.2 Brake thermal Efficiency (BTE)

BTE evolutions of different fuels at different engine loads are presented in figure 4-2. TPO blends use on engine results on a higher BTE reaching 3 points at full load with C125. The lower efficiency while using diesel fuel can be related to its shorter ID which leads to an earlier pressure rise during compression stroke and increases pumping work. At 25% load NRHR of both blend (C125 and C225) are identical which lead to identical values of BTE. With load increase, C225 has a sharper ascending premixing combustion as compared to C125, which leads also to higher pressure increasing rate during compression and a higher pumping work, which explains differences in engine efficiency while using both blends.

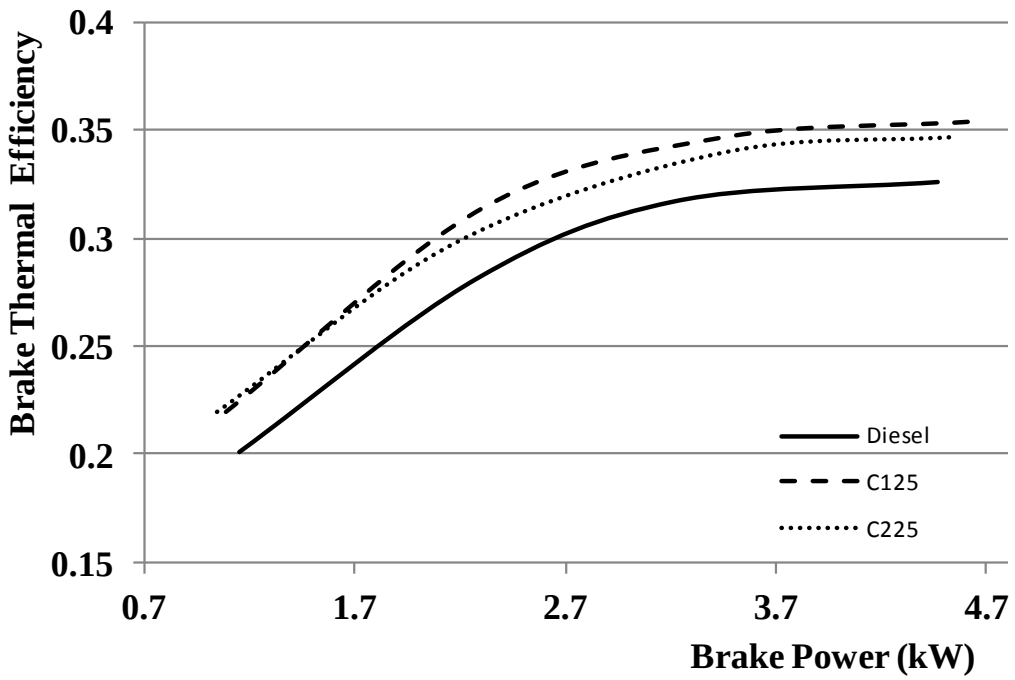


Figure 4-2, BTE of C125, C225 and Diesel

BTE; which evolves upward with the load increase; for both TPO combustibles, is better than those of diesel. This contradicts the result of Murugan et al [4] that the BTE of diesel is higher, and the result of Martinez et al [5] that both blended TPO and diesel have the same BTE at high load level.

From one side, comparing blended TPO combustibles with diesel, BTE depends on both LHV and viscosity [1,2,4, 5]. In this work, the higher BTE agrees with higher TPO viscosity, which stays lower than those of diesel. Low viscosity, as it has been mentioned in NRHR paragraph, improves the atomization process, which gives in better Fuel-air mixing. This leads to better combustion. Thus, the viscosity effect is the dominant factor in the performance of the studied combustible.

4.III.1.3 Brake Specific Fuel Consumption (BSFC)

Figure 4-3 illustrates the BSFC of the three combustibles. The relationship between BSFC and BTE is showed in equation 4-1.

$$BSFC = \frac{3600000}{BTE \times LHV} \qquad \text{Eq 4-1}$$

As it can be noticed BSFC depends on engine BTE and on fuels lower heating value. As it can be noticed, the effect of higher engine efficiency while using TPO

blends has a higher effect on BSFC than the lower fuels heating values. Thus, using TPO blends reduced engine consumption by 7.5% at low loads and 6.6% at high loads. Since C125 and C225 are having the same LHV, their BSFC trends represent the inverse of their BTE trends and the maximum difference between them does not exceed 2%.

The BSFC increase with load can be explained by the decrease of mechanical/pumping losses-to-fuel ratio [2,9].

The three combustibles have approximately the same performance in the engine with a slight advantage of blended TPO because of their low viscosity. In addition, no sulfur was detected in TPO (cf. GC/MS results), which contradicts some researches claiming the highest sulfur content of TPO [2,5,8,9].

At the end of this part, it can be concluded that engine performance is enhanced with TPO blends up to 25% with diesel fuel. Non-distilled TPO seems to be more attractive than distilled one in terms of engine efficiency and fuel consumption. On the other hand high premixed combustion of C225 could represent harmful effects on cylinder walls and piston head, like overheating. A complementary study was led on engine emissions in order to evaluate the global effect TPO blends use on diesel engines.

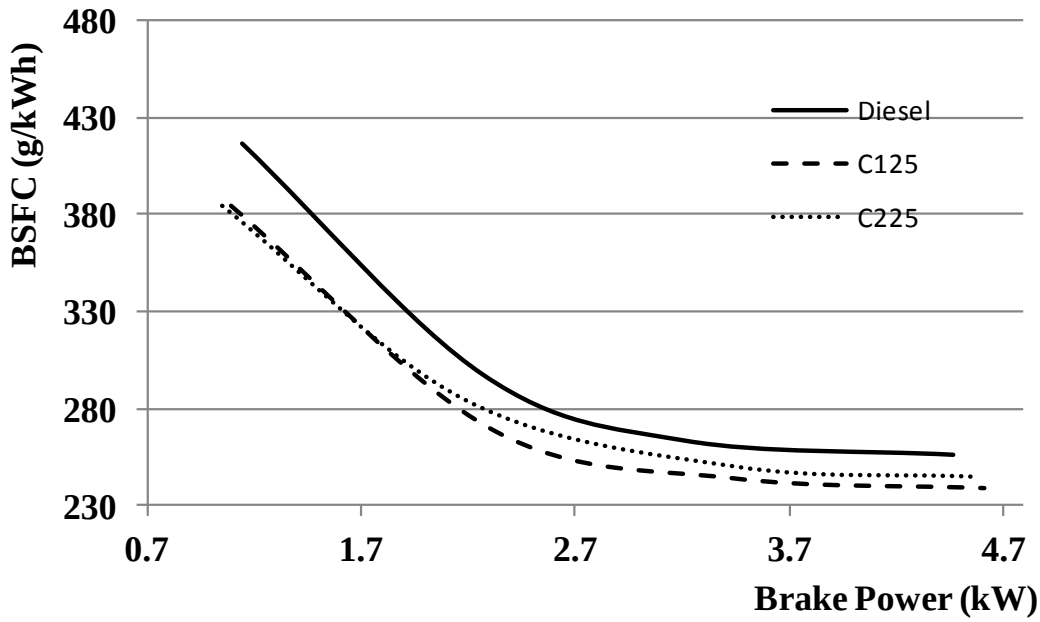


Figure 4-3, BSFC of C125, C225 and diesel.

4-III.2 Pollutants Emission

Gaseous emission plays an important role in deciding the workability of a combustible as a fuel. The main four major emissions are THC, CO, NOx and PM. They will be studied individually.

4-III.2.1 Total Hydrocarbons (THC) emission

THC (or called HC in some references) in the gaseous emission; due to either unburned hydrocarbons or partial thermal decomposing of some hydrocarbons; can result from different reasons like:

1) Over-mixing, where the fuel/air mixture becomes diluted with air, some zones of engine cylinder, called over-lean region, lay under the lower limit of inflammability and fuel escapes the burning zone leading to Unburned Hydrocarbons emission on the exhaust gas. This phenomenon is likely to occur at premixing combustion phase with volatile fuels and high excess of air.
2) Under-mixing, where fuel/air mixture is not homogeneous, and over-rich pockets of fuel are concentrated in burning zone, leading to partial combustion and to increase of THC in exhaust gas. This condition is more likely to occur during diffusion combustion where fuel has not enough time to mix with air oxygen. In this case, higher fuel viscosity increases THC.
3) Flame quenching occurs when flame meets cold walls of cylinder which leads to its extinction and to incomplete combustion conditions increasing THC production
4) The presence of heavy compounds (like tar) having lower ability to inflammation lead to thermal cracking instead of combustion and promotes THC emission.

THC emission for the three combustibles is showed in figure 4-4. It can be noticed that C125 has the higher emission rate among different fuels. This could be mainly referred to its higher tar content. Existed tar contains very heavy

compounds that either they aren't decomposed easily inside the engine chamber at the ambient conditions (residence time and temperature) or they are decomposed partially producing lighter compounds. Some of these lighter produced compounds are showed by Martinez et al [5] which are:

CH_4, C_2H_4, C_2H_2, CH_2O, C_2H_6, C_3H_8, C_5H_{12}, C_6H_6, HCOOH, HNCO, C_4H_6, C_8H_{18}, C_3H_6, 2-methylbutane, $C_2H_4O_2$, HCN, C_2H_4O, isobutane

C225 results in higher THC than diesel fuel at low loads. At this region combustion occurs mainly by premixing, thus, the lower viscosity of C225 enhances the formation of over-lean regions where fuel escapes burning zone and undergoes thermal cracking. With load increase, the increase of overall fuel/air ratio reduces the formation of over-lean areas. And on the other hand, diffusion combustion becomes more important. Thus, lower viscosity of C225 has less influence during premixing combustion and higher influence at diffusion combustion, where the better jet atomization reduces HTC formation which explains the smallest difference and even the inversion of trends between diesel fuel and C225 at higher engine loads.

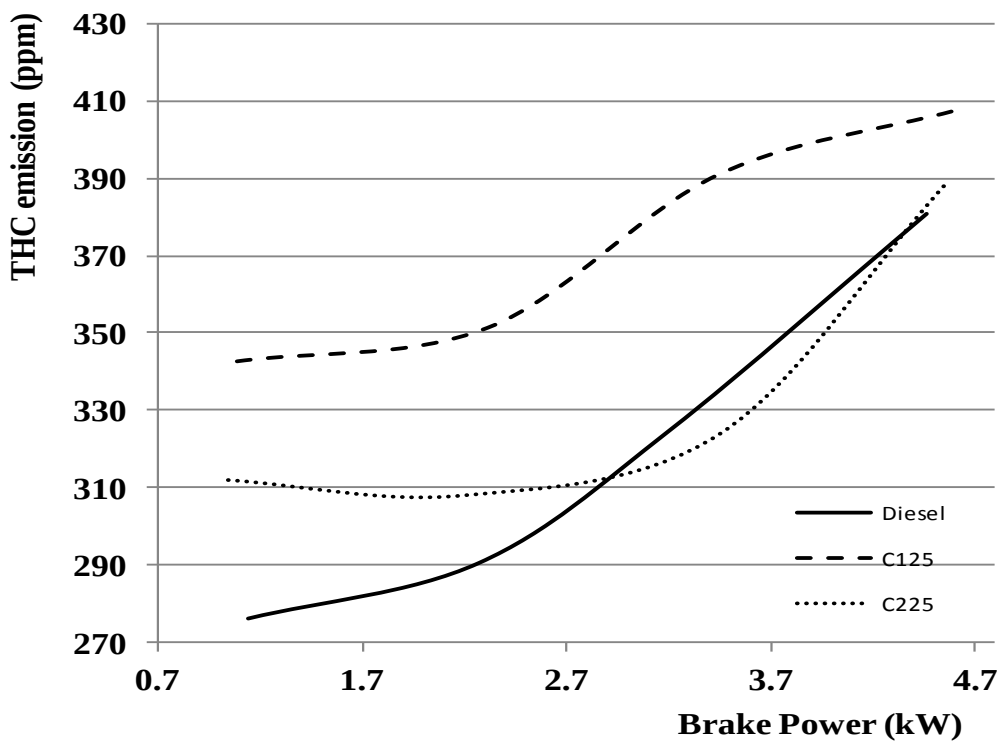


Figure 4-4, THC emission of C125, C225 and Diesel.

THC is increased with load level increment, it agrees with the work of Martinez et al [6], while at the same time; it disagrees with Frigo et al [9].

Many researchers [2, 4-6, 9] related the THC emission into physico-chemical characteristics as viscosity, volatility and PAHs content. This explanation is applied at the case of C225 with Diesel. In addition to these parameters, C125 THC emission is further increased because of tar content.

4-III.2.2 Carbon mono-Oxide (CO) emission

Carbon monoxide (CO) is the product of incomplete combustion in non-stoichiometric zones of fuel jet. Since diesel engine works with large air excess, CO emissions are produced in local fuel rich pockets in fuel jet during diffusion combustion. Fig 4-5 shows the evolution of CO emissions of different fuels with respect to engine load. At low loads, where combustion is almost achieved in premixing phase, CO levels are low and differences between different fuels emissions are negligible.

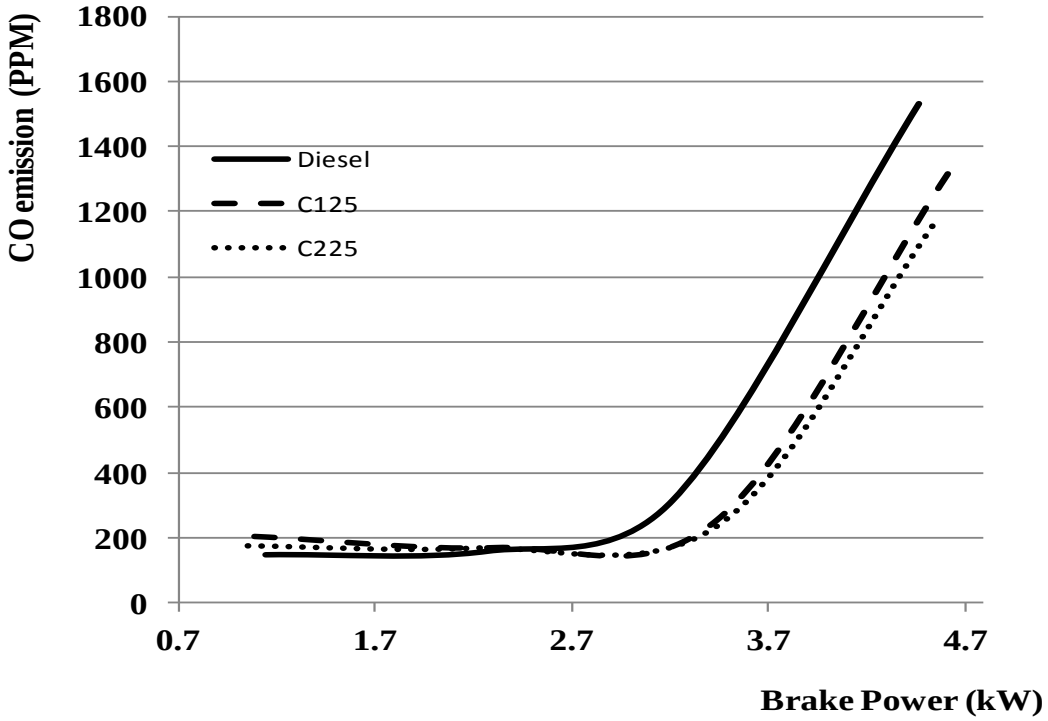


Figure 4-5, Co emission of C125, C225 and diesel.

At low loads, where combustion is almost achieved in premixing phase, CO levels are low and differences between different fuels emissions are negligible. With engine load increase, diesel fuel exhibits higher CO emissions than TPO blends. This could be explained by the lower viscosity of TPO blends, leading to higher atomization of fuel droplets and a better mixing with air. Unlike THC emissions and no differences in CO emission were noticed lead to think that the tar present in C125 is very difficult to be burned, and apparently, it undergoes thermal cracking rather than partial oxidation.

4-III.2.3 Nitrogen Oxides (NOx) emission

Nitric Oxides (NOx) are the result of three different types of reaction: thermal NOx, Fuel NOx and prompt NOx. Thermal NOx, the main source in diesel engine, results from the reaction of oxygen with air nitrogen at high temperatures and it is described by Zeldovic's mechanism. This kind of reactions is increased with temperature and oxygen concentration. Fuel NOx is produced nitrogen contained in fuel reacts with oxygen to form NO, thus this form is related to fuel content of N. finally the prompt NOx is formed during early combustion phases, where carbonated radicals of fuel react with atmospheric N_2 to form nitric compounds which on their turn undergo oxidation to form NO.

Figure 4-6 represents the evolutions of NOx emissions of different fuels at different engine loads. As it can be noticed, differences in emissions are very small to be considered. As equivalence ratios are almost the same while using different fuels at different load conditions, only cycle temperature can affect the production of thermal NOx. As it is difficult to calculate cycle temperature, it will be easier to compare cycle pressures as a reflection of temperature. Figure 4-7 illustrates the evolutions of in-cylinder maximum pressure evolutions of different fuels at different engine loads. C125 and Diesel fuel result on similar trends, however, C225 results in lower peak pressure at the whole load range. Thus it could be expected that diesel fuel and C125 have higher NOx emissions level than C225. So the thermal NOx alone cannot explain NOx trends, neither fuel bond NOx can because different fuels have the same N content. Thus, the higher premixed phase

of C225 can lead to think that prompt NOx is largely formed at this region which compensates the effect of lower temperature on the reduction of thermal NOx production.

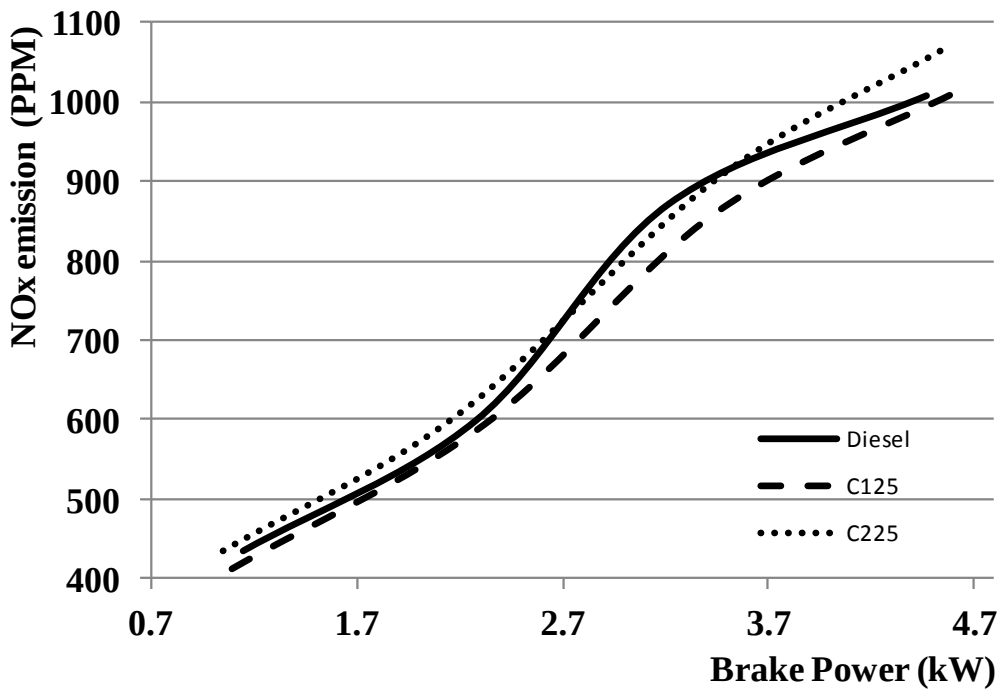


Figure 4-6, NOx emission of C125, C225 and Diesel.

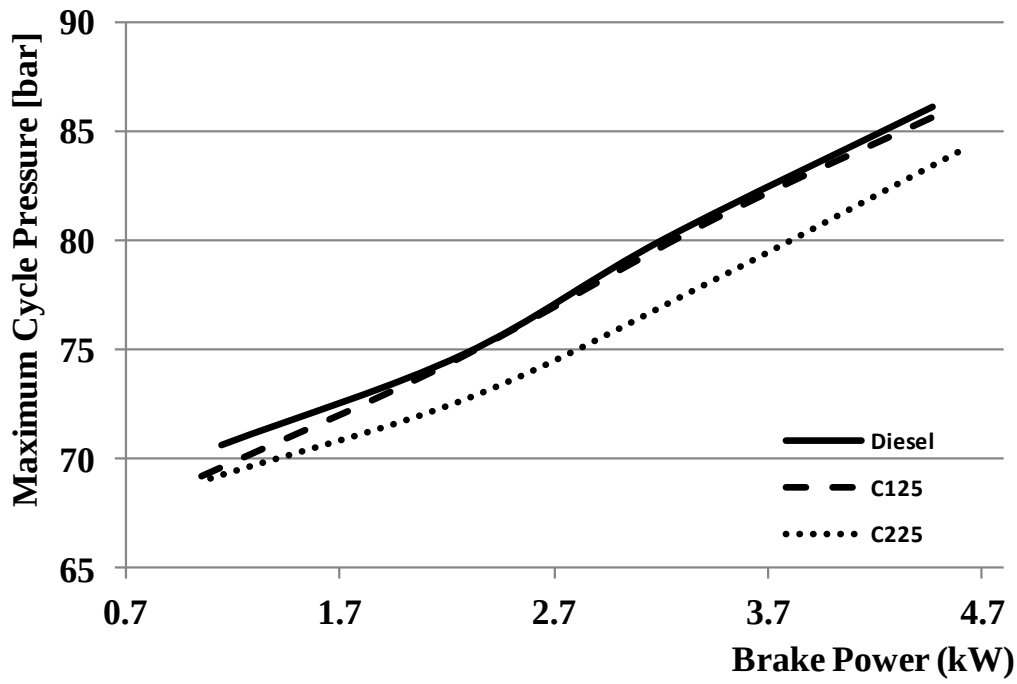


Figure 4-7, Pressure Cycle .

4-III.2.4 Particles Matter (PM) emission

Actually, as aforementioned for other types of emission, there are many parameters affecting the PM emission. PM consists mainly of the solid particles. These solid particles are carried as suspended in the liquid, or they are produced during the combustion inside the engine (especially the carbon soot) [4, 5, 12]. Indeed, unburned compounds which leave the combustion chamber form part of PM.

During combustion produced PM is created by thermal cracking of fuel in the zones deprived of oxygen. The PM are the solid product of fuel pyrolysis and it is increasing with the increase in C/H and C/O ratios and with the presence of aromatic and polyaromatic components**,** it also increases with the equivalence ratio and the cycle temperature. After its formation, PM starts mixing with air oxygen again during expansion phase, if burned gas temperature is high enough, PM undergoes oxidization process and emissions will be reduced. PM emitted in exhaust gas are the difference between created and oxidized PM.

Figure 4-8 illustrates the evolutions of PM emissions of different fuels at different loads. As it can be noticed, different fuels result in increasing trend with respect to engine load because of increasing equivalence ratio. However PM resulting from each fuel has its own trend of evolution. Diesel fuel and C125 resulting trends are almost similar with higher emissions for diesel fuel. On the other hand, C225 results on lower variation rate with almost a linear trend. This linear trend can be explained using NRHR curves, where the increase of diffusion combustion area with engine load is less important than other fuels. As it was aforementioned, diffusion combustion is the main reason of PM production, thus its trend with respect to load is reflected in PM emission trend.

Referring to chemical composition, it could be expected that C125 and C225 result in similar PM emission trends with a higher shift for C125. But experiments show different trends and inversed magnitudes. In order to explain this issue, trends of HRRN of C125 and C225 should be examined. C225 burns sharply at premixed phase and then less fuel is available to burn at diffusion phase, leading to lower late combustion temperature, which explains its higher PM emissions. C125, although

its higher diffusion combustion (main source of PM formation), produced PM stays for a longer time period at high temperature, where it mixes with air oxygen and undergoes a considerable reduction. C125 and diesel fuel have almost the same diffusion combustion profile, however, the lower viscosity of C125, led to a lower formation of PM which explains its trend.

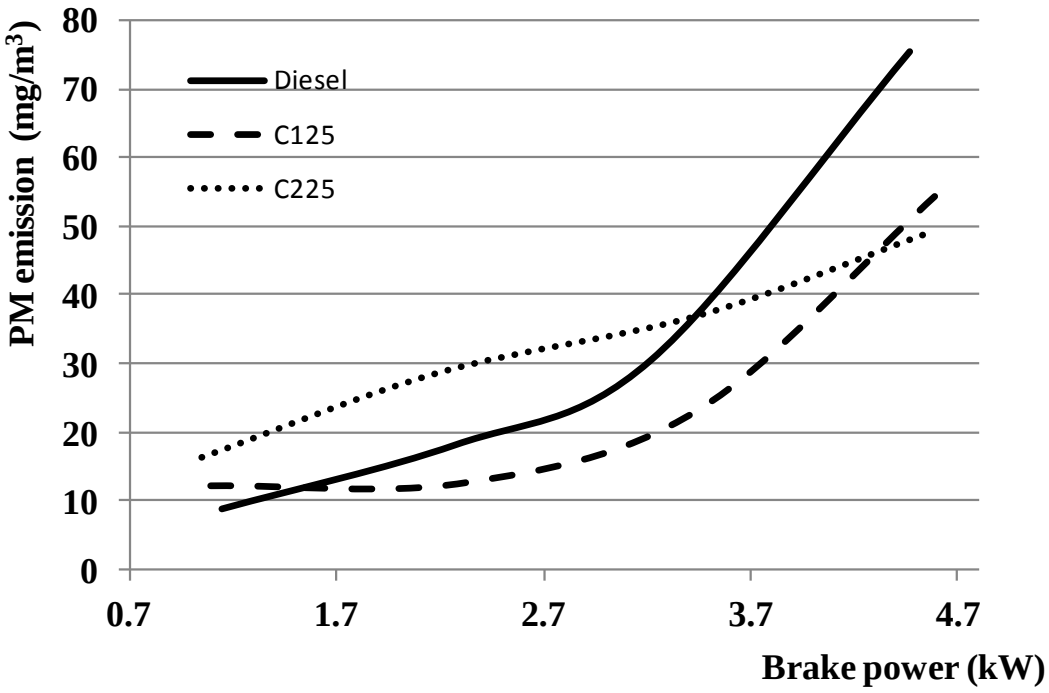


Figure 4-8, PM emission of C125, C225 and Diesel.

4-IV Recovery of Energy

Using 650W resistance to pyrolysis ≈1200 g of scrap tires during 237.5 minutes consumes 2.6 KWh. As the liquid yield is 42.82% (table 3-19) with LHV 40.9 MJ/Kg table (4-4). Then the theoretical produced energy is:

$$\text{Theoretical Produced energy} = 1200 \times \frac{42{,}82}{100} \times \frac{40{,}9}{1000} \times \frac{1}{3{,}6} = 5.83 \quad Kwh$$

Which is 2.25 times higher produced energy than thus of consumed with regardless the energetic value of produced gas which is sufficient to achieve the whole pyrolysis process (ref 2, 3, 4 in chapter 3) in addition to the solid product if

it will be used as a solid combustible. It means that process pyrolysis with the aforementioned conditions is favorable from the energetic point of view.

4-V Conclusion

C125 is considered the best from the energy point of view as its BTE and BSFC are the best in comparison with other two examined combustibles. In addition, its gaseous emissions are comparable with those of commercial diesel. So it is encouraging to produce TPO in the aforementioned conditions (650W and without nitrogen) and used it in engine diesel with 25% blending.

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Chapter 5 Conclusion & Perspectives

V-I General conclusion

The Production of tire pyrolysis oil (TPO) from scrap tire with good characteristic (HHV, viscosity, density, flash point, tar content, S content……..etc.) requires working under mild conditions of input energy, temperature and inert gas carrier.

Firstly, it is sufficient to purge the inert gas carrier for 30 minutes before the pyrolysis process in order to get rid of the oxidative gases (i.e. O_2 and H_2O) out the reactor avoiding any oxidation process during the pyrolysis. Then the process could be started and the volatile matters (condensable and non-condensable) could push themselves under the force of evaporation process. The decomposable products (volatiles) evaporate under the influence of their boiling points, and sometimes at lower temperature under the influenced of pushing by lighter evaporated ones. But, what is more important is, that the heavier decomposable compounds remain inside the reactor exposing to another side cracking converting into lighter compounds which are favorable in the liquid product. While the presence of inert gas current will carry these heavy compounds easily and rapidly out of the reactor worsening the liquid product quality (tar).

Secondly, mild input heating energy (650W electrical input); which reflects in very low heating rate; helps to crack chemical bonds slightly giving free radicals; especially $S^{\bullet}$ and $H^{\bullet}$; sufficient time to react together again forming H_2S instead of transferring sulfur into liquid product. In addition, another free radical will react as well with each other producing light and not heavy molecules working as good alternative fuel or feedstock in the industry.

Thirdly, 475°C is enough to finish the pyrolysis process with good yield of pyrolytic products quantitatively and qualitatively. 475°C is lower than the other works' temperatures found in the literature (arriving to 800°C), in this case, saving time and energy decomposing process happened.

Finally, the produced liquid can be used as alternative fuel in the IC engine blending with commercial diesel up to 25% without any modification in the engine or any post pyrolysis treatment as distillation or add additives.

V-II Perspectives

To complete and improve this work, some other works should be done

1- Characterization of the solid and gas products,
2- Treatment of sulfur in the solid and gas products (it has been done partially),
3- Study the pyrolysis with distillation tower (column) at the exit of the reactor helping to separate the volatiles into many fractions. Each fraction has its own applications,
4- Study the pyrolysis in series of reactors, the output gas, which contains H_2 and CH_4 mainly, enters inside the next reactor helping the adding and hydrogenation reactions to take place. in this case, the percentage of both linear and saturated compounds increases dramatically improving the liquid product quality and quantity.

Thèse de Doctorat

Radwan ALKHATIB

Development of an alternative fuel from waste of used tires by pyrolysis

Développement d'un carburant alternatif à partir des déchets de pneus usagés par pyrolyse

Résumé

L'objective de ce travail est de valoriser des déchets de pneus usagés par pyrolyse afin d'obtenir un nouveau carburant comparable avec le gazole suivant la norme EN590. L'obtention de ce carburant était réalisée via l'optimisation des conditions de pyrolyse qui sont la température, la vitesse de chauffage (puissance de la résistance électrique) et du débit d'azote. Les valeurs optimales sont 465°C, 650 Watts et sans azote. Le rôle de l'azote est limité à purger le réacteur avant le début de la pyrolyse pour 30 minutes pour chasser tous les gazes oxydatives hors du système. Le carburant produit est comparable au gazole avec un pouvoir calorifique de 45 MJ/kg, une densité de 0.85 et une teneur en goudron 7%.

Mots clés

Pyrolyse, pneus usagés.

Abstract

The objective of this work is to get alternative fuel comparable with the available diesel in the market following the EN590. The fuel getting was via optimization of pyrolysis conditions which are temperature, heating rate (power of electrical resistance) and inert gas flow rate. The optimum values are 465°C, 650 Watts and without inert gas flow rate. Inert gas role is limited to purge the system for 30 minutes before start the pyrolysis to get rid of oxidative gases. The obtained product is comparable with the diesel as it has GCV 45 KJ/kg, low density of 0.85 and 7% tar content.

Key Words

Pyrolysis, waste tires.

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