Plant-based (Camelina Sativa) biodiesel manufacturing using the technology of Instant Controlled pressure Drop (DIC) : process performance and biofuel quality

Fanar Bamerni

To cite this version:

Fanar Bamerni. Plant-based (Camelina Sativa) biodiesel manufacturing using the technology of Instant Controlled pressure Drop (DIC) : process performance and biofuel quality. Chemical and Process Engineering. Université de La Rochelle, 2018. English. NNT : 2018LAROS004 . tel-02009827

HAL Id: tel-02009827

https://theses.hal.science/tel-02009827

Submitted on 6 Feb 2019

NIVERSITÉ DE LA ROCHELLE

UFR des SCIENCES et TECHNOLOGIE

Année: 2018

Numéro attribué par la bibliothèque:

THÈSE

pour obtenir le grade de
DOCTEUR
de
L'UNIVERSITÉ DE LA ROCHELLE
Discipline : Génie des Procédés Industriels
Présentée et soutenue par

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Le 23 février 2018

TITRE:

Procédé de Fabrication de Biodiesel assistée par Texturation par Détente Instantanée Contrôlée (DIC) de *Camelina Sativa* : Performance des Procédés et Qualité du Produit.

Plant-Based (Camelina Sativa) Biodiesel Manufacturing Using the Technology of Instant Controlled Pressure Drop (DIC); Process performance and biofuel Quality.

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Dedication

To

My Merciful Mother ....

The Soul of My Father..

My Teachers...

My Dear Brother and Sisters ....

And All My Friends..

Fanar

ACKNOWLEDGEMENT

Great thanks to Allah, the most merciful, the most compassionate. It is my pleasure to express my deepest thanks and sincere gratitude to my supervisors Prof. Ibtisam Kamal and Prof. Karim Allaf for their advice, scientific suggestions, encouragement, kind assistance and continual guidance throughout the study period.

I also extend my gratitude to all the staff members in the University of La Rochelle. I also appreciate the efforts of all staff members in Zakho University. Specially the staff in Department of Chemistry at Faculty of Science.

My great thanks and respect to Dr. Yosef from Agriculture College and both of Dr. Jamal from chemistry Department and Dr. Deea from Biology Department at Faculty of Science from Dohuk University. I would like also to thank each of, Mr. Ali El-Tememy in the Ministry of Science and Technology/ Environment and Water Department/ Baghdad, and Mr. Ali Showani, in Kirkuk Refinery, for their help.

Finally, I would like to pass my sincere gratitude to my family and all my friends for their love, support and continued encouragement and assistance.

LIST OF PUBLICATIONS

1- F. Bamerni, I. Kamal, and K. Allaf, “Swell-Texturing assisted *in-situ* Transesterification of Camelina Seeds Biodiesel,” International Journal of Engineering Research and Development, vol. 13, no. 9, pp. 31–44, 2017.

2- F. Bamerni, I. Kamal, and K. Allaf, “Coupling of Texturing/Cooling Using Instant Controlled Pressure Drop and Transesterification for Biodiesel Production from *Camelina Sativa*,” Global Journal of Researches in Engineering, Vol. 17 no. 2 Version 1.0, 2017.

3- F. Bamerni, I. Kamal, and K. Allaf, “How can “Instantaneous Pressure-Drop DIC” Texture Camelina Seeds, Increase Extraction Yields and Preserve Vegetal Oil Quality?” Global Advanced Research Journal of Engineering, Technology and Innovation, Vol. 6 (1) pp. 001-011, January, 2018.

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LIST OF ABBREVIATIONS

Abbreviation	Full Name
DIC	Instant Controlled Pressure-Drop
RSM	Response Surface Method
$Y_{Solvent}$	yield of solvent extraction for seeds
$Y_{pressing}$	yield of pressing extraction for seeds
Y_{meal}	yield of solvent extraction for meal
T	Temperature
T	Time
Db	Dry Basis
Wb	Wet Basis
Ddb	dry dry basis
ISTE	*In-situ* Transesterification
TE	Transesterification
ISTE/DIC	In situ transesterification process coupled with Instant Controlled Pressure-Drop treatment
TE/DIC	Transesterification process coupled with Instant Controlled Pressure-Drop treatment
Camelina s.	*Camelina sativa*
FAMEs	Fatty Acid Methyl Esters
ASTM	American Society for Testing Materials
UNE-EN	European Committee for Standardization
FFA	Free Fatty Acids

FA	Fatty Acids
BC	Before Christ
AD	After Jesus was born
LA	Linoleic Acid
ALA	α-Linolenic Acid
GSL	Glucosinolates
FT	Fischer–Tropsch
HRJ	Hydro-Processed Renewable Jet
GD	Green Diesel
ISO	International Organization for Standardization
HHV	Higher Heating Value
GHG	Greenhouse Gas
FAEE	Fatty Acids Ethyl Ester
FABE	Fatty Acids Butyl Ester
UAE	Ultrasound-Assisted Extraction
MAE	Microwave-Assisted Extraction
SFE	Supercritical Fluid Extraction
ASE	Acceleration Solvent Extraction
EAE	Enzymatic-Assisted Extraction
TAG	Triglyceride
cSt	Centistoke
DoE	Design of Experiment
API	American Petroleum Institute

IP	Standard Test Methods of UK
DIN	Standard Test Methods of Germany
AFNOR	Standard Test Methods of France
AATCC	American Association of Textile Chemists and Colorists
CFPP	Cold Filter Plugging Point
EN	Equivalent European Standard
RI	Refractive Index
IN	Iodine Number
SV	Saponification Value
SFA	Saturated Fatty Acids
USFA	Un-Saturated Fatty Acids
MUFA	Mono-Unsaturated Fatty Acids
PUFA	Poly-Unsaturated Fatty Acids
ANOVA	Analysis of Variance
CN	Cetane Number
CP	Cloud point
PP	Pour point
FP	Freezing point
rpm	revolutions per minutes

ABSTRACT

Camelina sativa seeds (0.0420 g H_2O/g db (dry basis)) moisture content were treated by the thermo-mechanical; high temperature-short time Instant Controlled Pressure-Drop (DIC) as a texturing pretreatment step at different DIC operating parameters, followed by oil extraction process. Two different techniques of extraction of the vegetal oil, i.e. mechanical pressing and solvent extraction were carried out including the definition of the intensification routes. The DIC process showed highly positive effect on oil extraction yield. Optimizations of DIC parameters; temperature (T) and time (t) for the two oil extraction pathways were computed using Response Surface Method (RSM). The Response Surface Modeling (RSM) results predicted maximized yield of oil extraction by pressing and using solvent while lower oil extraction yield from the pressing cake using solvent. The optimum oil yield was up to 0.3153 and 0.4490 g oil/g db (dry basis) from pressing and solvent extraction respectively compared to 0.2277 and 0.368 g oil/g db, from the crude raw Camelina seeds, thus DIC allowed the yield to increase by 38% and 22%, respectively by DIC treatment at optimum operating conditions (157.7 ºC for 40.6 s).

The physical properties of the oils extracted were determined and compared with those reported in literatures. The results showed that the quality of the oil extracted from the DIC textured seeds was similar to that extracted from the raw seeds. The fatty acid profile of Camelina oils was determined by GC-FID (Gas chromatography – Flame Ionization Detector). The GC-FID analysis revealed that the main fatty acids content (wt. %) of the oil from un-textured Camelina seeds were; (6.15%) Stearic acid, (13.54) Linoleic acid, (16.50%) Palmitic acid, (21.83%) Linolenic acid and (32.50%) Oleic acid, compared to (6.22%) Stearic acid, (14.47%) Linoleic acid, (17.70%) Palmitic acid, (21.48%) Linolenic acid and (34.01%) Oleic acid from the DIC-textured seeds.

In the present work, an intensified way for biodiesel manufacturing was investigated. The innovative route involves coupling the texturing process by DIC with acid catalyzed transesterification (TE) and *in-situ* transesterification (ISTE) processes. Adequate Experimental Designs using Response Surface Methodology (RSM) were adopted to optimize and model mathematically the effect of biodiesel manufacturing variables

and the effect of DIC operating variables on biodiesel yield. The experimental designs were adopted after preliminary laboratory experiments.

The optimized conditions of TE of the un-textured Camelina oils were found to be: reaction time (36.6 minute), catalyst [H_2SO_4]/ solvent [Methanol: Toluene (90:10)] (2% v/v), and solvent/oil ratio (17:1 v/v). The optimized conditions of TE were implemented to study the impact of DIC operating parameters; saturated steam temperature (T) and processing texturing time (t) as independent variables on the yield of biodiesel (Fatty Acid Methyl Esters) (FAMEs). The biodiesel yields from the raw and DIC textured seeds were of approximate values: 0.9991 g FMEs/g db oil (dry basis) from DIC textured seeds, compared to 0.9649 g FMEs/g db oil from raw un-treated seeds. The similar oil source may be behind the close biodiesel yields. The results of GC-FID approved the situation, such as no remarkable differences were predicted for the chemical and physical properties for the oils extracted from the raw un-textured and DIC-textured seeds.

Then optimized conditions for ISTE process for the raw seeds were estimated using RSM. The optimum operating variables were catalyst: solvent (10% v/v), and solvent/seeds ratio (50:1 v/wt.). These optimized conditions of ISTE were implemented to study the impact of operating parameters of DIC texturing using saturated steam temperature (T) and processing texturing time (t) as independent variables on the yield of Fatty Acid Methyl Esters (FAMEs) as dependent variable. The new DIC/ ISTE process resulted in acquiring a yield of 0.7731 g FMEs/g ddb (dry dry basis) compared to 0.3935 g FAMEs/g ddb from raw un-treated seeds.

The physical properties for FAMEs produced in the current work by transesterification and *in-situ* transesterification processes at optimum conditions for DIC-texturing for Camelina seeds were determined and compared with ASTM D 6751-09 and UNE-EN 14214 standards. The results confirmed that almost all the properties of FAMEs produced in the current work within the standards limit. An exception was detected for Iodine value, which show as a greater value than the value limited by ASTM D 6751-09 and UNE-EN 14214. The higher iodine value maybe attributed to high content of unsaturated methyl esters in Camelina biodiesel. The value of the properties of DIC-Camelina biodiesel had been compared with the values obtained by other researches.

The kinetics of the transformation process to biodiesel for ISTE and DIC/ ISTE were followed by Gas chromatography. Samples from the reaction pots withdrawn after (0.5, 1, 2 hours) reaction time were analyzed directly by GC-FID. The results confirmed that FAMEs produced by DIC/ISTE have higher FAMEs yield compared to those via conventional ISTE.

A comparative study of an industrial production of biodiesel using 1000 kg of Camelina seeds was performed in the current work. Conventional Transesterification TE of Camelina oil, and *in-situ* transesterification ISTE of un-textured raw seeds and the DIC-textured seeds resulted in great difference in biodiesel yield. An increase in biodiesel yield of about 86.56 and 155.80 kg/ 1000g is produced from TE and ISTE respectively. The findings are of potential importance from industrial point of view in term of cost effective biodiesel production.

CHAPTER 1. GENERAL INTRODUCTION

1.1 Fossil fuels and Biofuels

Today, the vast of the energy utilized in different life sectors originates from fossil fuels, for example, petroleum, coal, and natural gas. While fossil fuels are until now being formed by underground heat and pressure, they are being consumed more quickly than they are being made. Hence, fossil fuels are considered as a non-renewable or non-sustainable fuel; that is, they are not replaced as soon as we used it. Petroleum fuels formed from a hydrocarbon as a complex mixture with a trace amount of organic compounds, for example, nitrogen, oxygen, and sulfur as well as compounds containing metallic constituents, especially iron, vanadium, nickel, and copper. The renewable energy sources such as biomass, hydro, solar (thermal and photovoltaic), wind, geothermal, marine, and hydrogen will play an important role in the future [1] and [2].

There are two schools describe the origin of petroleum fuels: the first one is, a Western school suggesting that the petroleum fuels origin is biogenic producing from the decay of organic biological substance and stored in sedimentary basins close the Earth's surface. While the second school, Ukrainian-Russian school suggesting that the petroleum origin is abiogenic proposing that a lot of carbon found naturally in the planet, some in the form of hydrocarbons. Since the hydrocarbons are less dense than aqueous pore fluids thus it has the ability to migrate towards the up during profound break systems[3] and [4].

In general, petroleum is one of the more important substances consumed by the human at the present time. It is utilized as a major source of energy for heating, industry, and transportation and it also supplies the raw materials for the petrochemical plants to produce plastics, polymers, and many other products [5] and [6].

Despite the vast fall in price of fossil fuels, and due to consider the fossil fuels as a non-sustainable resource and its inevitable depletion feature, with addition to increase the environmental pollution day by day due to the large utilize of the low grade of petroleum oil, which liberate some amount of SO_x, CO_x, and NO_x to the atmosphere.

As a results, biodiesel promises to be the fuel of future due to its favorable environmental features and there have been generous increments in biodiesel production in recent years and this trend is predicted to continue, that is leaded to that the alternative fuel and bio will take a more important role as the world energy supply for future life [7], [8] and [9].

The consideration of biofuels is expanding worldwide as substitutions for petroleum-derived transportation fuels to support global warming. The expression biofuel is utilized to mean any liquid fuel produced from plant material that can be utilized as a substitute for petroleum-derived fuel [10].

The most important biofuels generated from biomass are bioethanol and biodiesel [11].

In general, there are different feedstocks and conversion technologies can be utilized in biofuel production, bioethanol mostly is produced by fermenting plant carbohydrates with yeast, it is produced from sugar or the starch fraction of plants (e.g., Sugar Beet*,* Sugar Cane, Corn, Cassava and Wheat), also bioethanol can be produced from lignocellulosic materials. While biodiesel produced from vegetable oils (e.g., Palm oil, *S*unflower*,* Soybean and Rapeseed), animal fats and microorganisms, like microalgae [12] and [13].

1.2 Biodiesel

In recent years, the research on the production of biodiesel has increased significantly because of the demand for an alternative fuel which endows with renewability, biodegradability, and low toxicity. Animal fats, plant oils, microalgae oils and waste products such as, cooking oils, animal rendering, and fish processing waste have been employed as raw materials for biodiesel production. With a view to designing an environmentally and economically sustainable biodiesel production process, a proper understanding of the factors affecting the process and their relative significance is necessary [14].

Biodiesel has been defined by the American Society for Testing and Materials (ASTM) as a mixture of long-chain mono-alkyl esters from fatty acids derived from renewable resources, to be utilized in diesel engines [15]. According to the raw material used in the biodiesel production, historically the process was classified into first, second, third and fourth generations.

First generation biodiesel was directly related to the main use of edible oil seeds, food crops, and animal fats [16]. Thus, during this period, it has been noted that about (95%) of biofuel worldwide was derived from edible vegetable oils such as Canola and Soybeans, and a heated debate on 'fuel vs food' has condemned the competition between fuel production and feed - food uses [17]. Consequently, first generation biofuels were associated with a number of issues resulting in greatly increasing of food crops. This problem has favored the seeking of non-edible biomass for the production of biofuels [18].

Second-generation biodiesel has been indicated to specific biomass, such as wastes and by-products. It also proposed dedicated raw materials, short rotation forests and other energy crops. Nevertheless, such biomass would also need lands in competition with food production [19] and [20]. The problems with this generation were the costly advanced technology needed to develop cost-effective conversion of biomass to fuel [19], since even the residual cooking oil requires additional processes for purification [21].

The third-generation biofuel feedstock had concerned algal biomass (especially microalgae) [22], which has a very special growth yield as compared with first and second generations. Algae are known to produce biomass faster using reduced land surface. However, production of algal biomass presents technical challenges such as additional energy consumption for the cultivation of algae (mixing, filtration, centrifugation, etc.) and dewatering [19] and [21].

The fourth generation of biofuels has inserted the concept of “cell factory”, based on studies of metabolic engineering of algae to increase the photosynthetic ability of the cell to produce more yield of fuel [23]. This 4th generation has also the advantage to not imply competition with food nor food land. However, their actual applications in the industrial scale field stay limited because of technological barriers. Actually, such biofuel production has not been evolved to completely function in oxygenic photosynthetic organisms, and its performance has not been optimized. So, there are no matter what novel fuel molecules could be made from algae, it is despairing to make an impact on the fuel market until the technology is economically feasible [24] and [21].

The eventual fate of biofuels may not depend exclusively on one generation, but rather might be a combination of the three generations to cope with increased worldwide demand because of depletion in the world's oil resources [21].

1.3 Biodiesel Production

Since the vegetable oils can be utilized directly as biodiesel, while due to their high viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains. Direct use of vegetable oil in diesel engines in isolation is technically not possible, leads to appear problems only after the engine has been working on vegetable oils for longer periods of time, particularly with direct-injection engines [25], [26] and [1]. example for the problems caused by the direct use of this high viscos vegetable oils and fats in diesel engine is, its leads to deposits on various engine parts with addition to several other operational problems [27].

The problems have been qualified by developing vegetable oil derivatives that approximate the characteristic and performance and make them appropriate with the hydrocarbon-based diesel fuels through different methods [28] including: Dilution [28], Micro-emulsion of oils [26] and [29], Pyrolysis of Biomass [1] and [30], Transesterification [31], [32] and [33] and *in-situ* transesterification [34] and [35].

1.4 Biodiesel Raw Materials

Recently, biodiesel has become more attractive because of its environmental advantages and the fact that it is formed from renewable resources [36].

Biodiesel price is directly related to the cost of the used raw materials (70-95 % of the total biodiesel cost) [16]. According to USA report for biodiesel production in 2016, mentioned that the Soybean oil remained the largest biodiesel feedstock during December 2016 with 610 million pounds consumed, also reported the others raw material which used in this production were vegetable oils such as (Canola, Corn, Cottonseed and Palm) and animal fats such as (poultry, white grease and tallow) and recycled feeds such as (yellow grease) [37].

Finally microalgae also can be used as a feedstock in this production [23] and [38].

Used Soybean seeds or oil has some drawbacks in biodiesel production like, high cost of its seeds and the Soybeans have only 18-20% oil content in addition to that the Soybean oil is the major edible oil in the world [39].

Jatropha curcas is another feedstock which widely used in worldwide to produce biodiesel [40] and [41], while it is not a food crop and the oil is non-edible. but it is consider as a one of poisonous crops and the most of the Jatropha which currently grown is a toxic, thus it is make the seed-cake unacceptable for use as cattle feed and may effect on a human safety hazard [39].

In the current research, the possibility of producing biodiesel from Camelina seeds have been studied. This feedstock can be classified as a new generation or a more relevant second-generation type. Camelina have been classified and selected according to several factors; Camelina can be grown in short marginal periods without being a competitor of food land since it can be used as a natural fertilizer when it is combined with edible crops on good arable land. On the other hand, life-cycle evaluations of biodiesel produced from Camelina grown under different conditions showed a reduction in energy inputs and overall greenhouse gas emissions compared to diesel, as well as other biodiesel oleaginous crops [42], [43] and [44].

Furthermore, it was reported that the optimized Camelina biodiesel respond with the ASTM D6571 and EN 14214 standards regarded to biodiesel and are comparable to those of regular diesel fuels [45] and [46].

1.5 Aim of the Current Study

The aim behind the current work is to establish a base for exploitation the natural renewable agro sources in Kurdistan region for production of biodiesel as alternative to fossil diesel fuel. Camelina seeds was chosen as a candidate renewable feedstock. It is a type of second generation for biodiesel, it is a non-edible crop, can be cultivated on marginal land.

An innovative technology mainly used as texturing process; the Instant Controlled Pressure Drop (DIC) was applied on the candidate feedstock for the purpose of enhancing the oil extractability and the yield of biodiesel. The impact of DIC treatment for *Camelina sativa* seeds on oil extraction and conversion to biodiesel throughout the conventional transesterification of the extracted oil, and *in-situ* transesterification of the seeds was studied using Response Surface Methodology. The optimized conditions of the conversion reactions as well as the DIC process for optimum texturing were estimated, and the corresponding mathematical models were adopted.

The extracted oils were characterized and the properties of Camelina biodiesel (FAMEs) were evaluated to identify the quality of the produced biodiesel and highlight the effect of DIC treatment on biodiesel quality.

CHAPTER 2. STATE-OF–THE-ART

2.1 Camelina Sativa

Camelina *(Camelina sativa L.)* is a cruciferous oilseed plant belonging to the Brassicaceae (mustard) family with the common names *false flax* and *gold of pleasure.* Seeds of the crop have been found in archaeological excavations in *Scandinavia* and *Europe*, were revealed the existence of *Camelina sativa (L.)* Crantz, C.microcarpa and C.linicola in the Bronze Age (1500-400 B.C.) and Iron Age (400 B.C.-500 A.D.) [47], [48] and [49].

Camelina sativa has important agronomic traits that recommend it as a perfect production platform for biofuels and industrial feedstocks [42].

Nowadays it gained a growing interest due to its high oil content, *Camelina sativa* is an oilseed crop that is currently being commercially produced in the USA as a feedstock for biodiesel [50], [51], [52] and [45].

Camelina possesses a short-season crop; (85-100 days) for example, Camelina matures 21 days earlier than *Flax* seed, It is a promising sustainable alternative energy crop because it can be grown as an annual summer or biannual winter crop under different climatic and soil conditions with the exception of heavy clay and organic soil [45], [51] and [53].

Recently, interest in *Camelina sativa* has been renewed due to the fact that the crop can be grown on poorer soils that require lower inputs of fertilizers and pesticides than traditional crops (Rapeseed/ Canola, Soybean*s* or *S*unflower*s*) required, it grows well in semiarid regions. Moreover, Camelina needs little water and does not compete with food crops [52] and [53].

To improve the health of the soil, *Camelina sativa* may be used as a rotation crop during the fallow years with wheat [54], and dryland cereals, like *oats* and *barley*, without affecting the yield of these crops. The roughly 5-7 million acres of land available through such a fallow rotation would provide a Camelina oil yield of 750-1000 million gallons per year. Yield produced of (Camelina – Soybean*)* and (Camelina – *S*unflower*)* were 82% and 72% respectively of their mono cropped counterparts however the net economic returns for (Camelina - Soybean*)* double crop were higher than Soybean alone. In a subsequent study, winter Camelina grown as double crop and relay crop with Soybean showed a similar net economic returns compared to the mono- cropped full season Soybean [42].

It is worth mentioning that the oil yield (L/ha) for Camelina, Rapeseed, Soybean and *S*unflower were reported as (106-907), (965-1342), (247-562) and (500-750) [55], while the seed yields (t/ha) for Camelina, Rapeseed, Soybean and *S*unflower were (0.90-2.24), (2.68-3.39), (2.14-2.84) and (1.44-1.70) respectively [55].

2.1.1 Geographical Distribution of *Camelina Sativa*

Camelina sativa originated in Germany and its cultivation expanding to Central Europe [56]. From the outset of 20th century up to the 1930's *Camelina sativa* was planted sporadically in France, Belgium, Holland, the Balkans and Russia. In 1950s Camelina was still planted in Sweden and it was an important crop in the USSR (Union of Soviet Socialist Republics) [48].

The popularity of Camelina waned after World War II since it was expensive and difficult to hydrogenate Camelina oil as other oilseed crops like Canola and Soybean which started gaining in popularity [57] and [43].

Camelina sativa has been traditionally cultivated in Europe as an oilseed crop to produce vegetable oil and animal feed. There is abundant archeological proof to show it has been planted in Europe for at least 3000 years. Camelina was an important oil crop in eastern and central *Europe*, and has continued to be cultivated for its seed [58].

Camelina seeds were discovered in a storage vessel in Eastern Turkey dating from (700 to 900 BCE) and in Romania in the transition from the Eneolithic to Bronze Age, showing that Camelina was likely cultivated for its oil. Though its importance decreased in the Medieval Age, in general, Camelina cultivation continued in sporadically form over the years [59] and [60].

finally, it is worth mentioning that the Camelina genus includes about 10 species, only *Camelina Rumelica* has existed in Iraq [61].

2.1.2 Description of *Camelina Sativa* Plant

Camelina sativa, has shallow root system, it's become woody as the plant matures and can grow to heights ranging from (30 to 80) cm [43]. Stems are generally smooth or only sparsely hairy near their base [62]. Camelina leaves are arrow-shaped, pointed with smooth edges and are (5 to 9) cm long [43]. It produces prolific small, pale yellow or greenish-yellow flowers with four petals [63].

The yellow flowers are very small (about 5 mm diameter) and self-pollination is predominant. The fruits are pear- shaped pods that contain (10–25) yellow-reddish seeds [64]. Various oilseed rape the pods are more or less shatter-proof, which makes Camelina much less weather-dependent, give rise to more consistent harvested yield [50].

Camelina seeds are very small that close to 1000 seeds weigh 1.0 g depending on the diversity and growth conditions, the color of the seeds was pale yellow-brown, turns dark-brown or reddish on ripening and under storage,

Figure 2-1 [51].

Figure 2-1. Camelina sativa *seeds*

2.1.3 *Camelina Sativa* Products

2.1.3.1 Camelina Seed Oil

The main product of *Camelina sativa* is the oil produced by crushing and pressing the seeds, the oil content of Camelina seeds ranged from 29.9 to 38.3% [52] and [56], however the oil values as high as 48% has been reported [43].

Free fatty acids (FFA) present in Camelina oil in the range between 0.55 to 0.80 % [51]. Over 50% of the fatty acids in Camelina seed oil are polyunsaturated acids is slightly higher than those published for some other vegetable oils [54]. The content of polyunsaturated fatty acids, such as linoleic acid (18:2 n-6) (LA) is about 15%, and the content of α-linolenic acid (18:3 n-3) (ALA) is about 38% [65].

while common vegetable oils such as Olive, Corn and *S*unflower oils have less than 1 % of α -linolenic acid, Rapeseed or Soybean oil have about 8 %, and Linseed oil with up to 60 % is the richest source of α-linolenic acid [52].

Camelina oil differed from the others in several respects. It was the only oil that contained 11-eicosenoic acid, and in relatively high concentrations (13.6%). It was somewhat higher in erucic acid than Flax (Linseed) oil but much lower than Crambe oil [56], this acid is considered as a limiting factor in vegetable oil because it determines the oil's applicability for human consumption. The permitted value of this acids is 5 % [52]. Table 2-1 illustrates the comparison of fatty acid percent content in Camelina from different researches.

The high degree of unsaturation renders Camelina oil highly prone to oxidation [42], in spite of that Camelina oil contains antioxidants (tocopherols, sterols, and polyphenols, which makes it more resistant to oxidation and give it a longer shelf life than Flax seed oil [53] and [66]. Tocopherol content is about 700 mg kg^{-1} [45].

Table 2-1. Camelina sativa *content of fatty acids from different researches*

Fatty Acids	**Content of Fatty Acid %**		
	[67]	[65]	[52]
Palmitic Acid (16:0)	5.5	5.33±0.05	6.43±0.01
Stearic Acid (18:0)	2.4	2.65±0.02	2.57±0.01
Oleic Acid (18:1)	14.4	13.4±0.13	17.40±0.30
Linoleic Acid (18:2)	19.1	14.8±0.12	16.90±0.10
α-Linolenic Acid (18:3)	33.5	37.8±0.17	35.20±0.40
Arachidic Acid (20:0)	1.5	1.25±0.02	1.24±0.05
Gondoic Acid (20:1)	15.0	15.4±0.16	14.90 ±0.20
Eicosadienoic Acid (20:2)	2.2	2.02±0.02	2.12±0.02
Eicosatrienoic Acid (20:3)	-	1.84±0.02	1.61±0.03
Erucic Acid (22:1)	3.1	2.76±0.07	1.62±0.03

It is worth mentioning that *Camelina sativa* composition varies with the agro technical measures (different regions and different growing conditions) used in their production. In different region, the fatty acid composition of Slovene Camelina oil was similar, but not the same as that reported for oils from seeds of Camelina cultivars grown in the USA, Central and Northern Europe [52]. The diversity values for fatty acids percent in Central and Northern Europe are reported in Table 2-2.

Table 2-2. The diversity values for fatty acids percent in Central and Northern Europe [52]

Fatty acids	Percentages in Central Europe	Percentages in Northern Europe
α-linolenic	34.9	39.7
oleic acid	14.0	16.9
linoleic acid	13.5	16.5
gondoic acid	15.1	15.8

in different climate, the fatty acids linoleic acid content recorded diverse from 12.4 ± 0.1 to 15.3 ± 0.4 in winter to summer, and α-Linolenic content recorded diverse from 40.8 ± 0.2 to 36.8 ± 0.8 in winter to summer [68].

Camelina oil is extracted from the seeds by various processes such as cold pressing [69], solvent extraction [53] or supercritical CO_2 extraction [70], Camelina oil, due to its relatively high (>50%) content in omega-3 and 6 fatty acids and low in saturated fatty acids, is considered to be a high quality edible oil [53].

Although *Camelina sativa* oil content of high amount of unsaturated fatty acids which make the oil highly prone to oxidation, but because of this oil also contains minor components, such as tocopherols, sterols, and polyphenols, some of which help to make the oil more resistant to oxidative rancidity, that's lead to make Camelina oil to be more stable towards oxidation than highly unsaturated Linseed oil but less stable than Rapeseed, Olive*,* Corn*,* Sesame and *S*unflower oils [53].

As reported that the oil content (wt. %) for Camelina, Rapeseed, Soybean and *S*unflower were 35-45, 40-44, 18-22 and 39-49 respectively [55]. In a comparison study between Camelina oil properties with Jatropha and waste cooking oil, it was shown that the Camelina oil had more suitable properties for biodiesel owing to:

- Viscosity; where the value of viscosity (mm^2/s) at 40ºC of the Camelina oil is 14.03, while for Jatropha oil and Waste oil are 20.5 and 28.8 respectively.

- Pour point; where the value of pour point (°C) of the Camelina oil is -23, while for Jatropha oil and Waste oil are 1 and -12 respectively.
- Acid value; where the value of acid value or number (mg of KOH/g) of the Camelina oil is 3.1635, while for Jatropha oil and Waste oil are 28.15 and 17.41 respectively [46].

2.1.3.2 Camelina Cake

Extraction of oil from oilseeds by pressing yield a by-product called Oil cakes/ meal which contain of 5-10 % residual oil, 13 % fiber, 5 % of minerals, some minor levels of vitamins [51] and [48], 40% protein and has a moderately-low glucosinolate (GSL) [71].

Glucosinolates are *β*-thioglucoside N-hydroxysulfates with a side chain and sulfur linked *β*-D-glucopyranose, GSLs are also anionic and sulfur-rich compounds that after hydrolysis by the enzyme thioglucosidase (called myrosinase) [72] which used as natural pesticides and as defense against herbivores; these substances are also responsible for the bitter or sharp taste of many cruciferous vegetables [58], Camelina meal, produces S*oy* quality meal and Canola quality oil [53].

However, the seed meal has not yet been allowed as animal feed according to Health Canada (Health Canada is the federal department responsible for helping Canadians maintain and improve their health). In Europe, *Camelina sativa* is listed as undesirable substances in animal feed. There is evidence that *Camelina sativa* seed meal used as feed 5 and 10% to broiler chickens resulted in decreased growth and feed intake, while it increased meat omega-3 fatty acid levels [73].

2.1.4 Potential Uses and Industrial Applications for Camelina

Ideally, crops grown for industrial feedstocks or biofuel purposes should not displace other crops grown for food. The agronomic features of Camelina mean that it is well convenient for this function. For example, its low water and fertilizer requirements mean it can be cultivated on marginal lands [42].

Camelina is a good alternative crop because it is, much less weather dependent, more consistent yield, and cheaper to produce than other new crops. Camelina has very low requirements for tillage and weed control [58] and [50].

Due to the unique fatty acid profile for Camelina, it is making it an ideal candidate for both industrial and nutritional applications. Historically, Camelina seeds were crushed and boiled to release oil used in food, lamp oil, medicinal purpose and in cosmetics purpose such as skin care products, soaps, and soft detergents [43].

The probable industrial applications of Camelina include its use in environmentally safe paintings, coatings, lubricants, resins, adhesives and low emission biodiesel fuels production. The oil extracted from Camelina seeds can be count as a good remedy for various medicinal issues. In classical medicine, it is utilized internally against stomach and intestine ulcers, digestive problems, colic attacks, and gastritis. Camelina oil can be useful for the regeneration of cells, skin flexibility and slenderness recovery. The fatty acid profile of Camelina makes it a suitable raw material for the production of cosmetic products such as; lotions, skin creams, balms, bars of soap, and lipsticks [45], [43], [74] and [51].

2.1.4.1 Human Foods

Camelina oil is reported to contain an unusually high level 188 mg/kg of cholesterol compared with other vegetable oils. Recently, cholesterol was reported to reach a level of 350 mg/kg in Camelina oil and a total sterol level of 5110 mg/kg, which is predominantly ß-sitosterol 59%. Tocopherol content in the oil was found to be 780 mg/ kg (mainly γ-tocopherol at about 92%) [54], and because of Camelina oils relatively high content in omega-3 (α-linolenic acid) fatty acids and low saturated fatty acids [53], the use of Camelina oil as a functional food oil is being developed in a variety of food products as an alternative to Linseed [54].

Camelina is being marketed in Europe as cooking oil and in salad dressing. Because the resistance to oxidation and the storage stability of Camelina oil is low at high temperatures, it is best suited for use in cold dishes and it is not suitable as deep-fat fry oil [75] and [45].

Camelina has two anti-nutritional factors, the presence of high erucic acid and glucosinolates which limits the amount of meal that can be fed makes higher dietary consumptions of Camelina oil unsafe [17] and [43].

2.1.4.2 Animal Feeds

In addition to use Camelina oil as an edible oil for human consumption, Camelina oil cake or meal can be used as a protein rich source as Animal feeds [45].

Defatted Camelina seeds meal include considerable levels of proteins and carbohydrates as well as a numeral of phytochemicals including glucosinolates, which could be used for additional agricultural, food and feed uses [58].

2.1.4.3 Camelina Oil as Feedstock for Renewable Jet Fuel

There are two widespread alternative fuel technologies for producing two sorts of jet fuels: Fischer–Tropsch (FT) fuels to displace the conventional kerosene fuels, and hydro-processed renewable jet (HRJ) fuels produced from hydro-processed oils [76].

Therefore, in order to enhance the cold flow properties of the fuels, isomerization to branched paraffin is decisive. Renewable jet fuels which made from vegetable oils initially requires hydro-deoxygenation identical to renewable diesel fuel. However, isomerization to branched paraffin to enhance cold flow properties is basically important in the case of jet fuel, according to ASTM D1655 (American standard for aviation turbine fuels), jet fuels must have freezing points below (-40°C). Simultaneously, paraffin is transformed to shorter-chain hydrocarbons by a selective catalytic cracking process, which leads to lowers the boiling range of jet fuel in comparison to that of diesel fuel. The resulting product is called hydro-processed renewable jet (HRJ) fuel [77] and [55].

Camelina's growing commercial prominence as a good alternative source to traditional petroleum derived jet and diesel fuels is demonstrated by a memorandum of understanding between 14 major airlines from the; United States, Canada, Germany, and Mexico announced by US-based Alt Air Fuels on negotiations to purchase 750 million gallons of renewable diesel and jet fuel derived from Camelina at Seattle-Tacoma International Airport [76].

Hydro-treated renewable jet fuel (HRJ) which derived from Camelina oil has been tested by the US military and a commercial airline and proved that this type of jet fuel satisfy stringent engine fuel and performance specifications, also reduced environmental emissions [78] and [79]. However, when Camelina based jet fuel compared with petroleum based jet fuel according to a life cycle analysis study, the carbon emissions were reduced to 84% [45].

In 2009 both Japan Airlines and KLM Royal Dutch Airlines successfully flight tested with 80% blended hydro-treated renewable jet fuel derived from Camelina oil. Camelina oil was extracted and processed to remove any impurities and then modified to a hydro-treated renewable jet and/or a Green diesel (GD) by hydrogen [80].

Additionally, Great Plains Oil & Exploration (LLC) and the Energy and Environmental Research Center at the University of North Dakota have composed into an agreement to produce combinations of diesel, jet fuel, gasoline and propane from Camelina [55].

2.1.4.4 Camelina Oil as Feedstock for Renewable Biodiesel

Camelina is known as a promising feedstock for biodiesel production. Camelina oil was methylated according to ISO 5509 standard (Animal and vegetable fats and oils - Preparation of methyl esters of fatty acids) [81].

Nowadays a major preoccupation is the production and usage of fuels obtained from renewable and eco-friendly sources. One option is the usage of vegetable oils which have a low contain of sulfur and aromatics and are totally biodegradable [82], and in order to sustain food production, oilseed crops should be from non-human food sources [43], currently, more than 95% of biodiesel worldwide is derived from edible vegetable oils such as Soybean*s* and Canola, which makes the biodiesel competes for grain with livestock and other food uses [17]. Another option is the usage of cheap feedstocks, due to the cost of feedstocks accounts for 75-85% of total biodiesel production cost [83]; for example, *Jatropha curcas* are require some irrigation for optimal growth and need to be supplemented with fertilizers to produce seed oil if grown on marginal lands [42], which makes them expensive and unattractive for biodiesel production. Therefore, it is important to develop non-edible and/or low-cost oil crops that meet certain requirements, including low agriculture inputs, high oil yield, and favorable fatty acid compositions, to increase the overall viability of biodiesel production [83].

The methyl ester produced from Camelina oil has properties similar to *Rape* methyl ester, with the exception of its higher iodine value which protects against more rapid deterioration of the lubricating oil [45]. A vehicle test in which high levels of lubricating oil dilution occurred gave no indication of any adverse effect of the high iodine value of the methyl-ester on lubricating oil properties [84]. Also it was found that the fuel properties (such as kinematic viscosity (40°C), flash point, cloud point, cold filter plugging point acid value, cetane number, and oil stability index) of Camelina biodiesel are similar to *S*unflower and Soybean biodiesel properties [43].

Since Camelina has high amount of erucic acid and glucosinolates, it is less competitive than other feed and food crops [17]. Also, Camelina has very low requirements for tillage and weed control. This could potentially allow this unique vegetable oil to be produced more cheaply than those from traditional oil crops such as Rapeseed, Corn, and Soybean [58]. In addition, Camelina has negligible potential as an invasive weed if grown in a large scale as biodiesel crop, all that makes Camelina seeds, an attractive crop for biofuels and many other industrial applications [46] and [43].

Camelina sativa biodiesel was evaluated as a viable biofuel alternative, a comprehensive characterization was performed based on the European and the American standards (EN 14214 and ASTM D6751) [85]. It has been shown that iodine value, cetane number and oxidative stability of Camelina oil derived biodiesel did not meet the quality specifications stipulated in the EN 14214 and ASTM D6751 standards [80]. However, It has been demonstrated that optimized biodiesel from Camelina met the related ASTM D6571 and EN 14214 biodiesel standards and can be used for diesel engines as qualified fuel [46]. Also, It was revealed that the fuel properties of biodiesel produced from *Camelina sativa* feedstocks meet the ASTM biodiesel standards and are comparable to those of the regular petroleum diesel fuels [45]. Table 2-3 shows the Camelina biodiesel properties compared with the properties of biofuel standard and petrodiesel fuel.

Table 2-3. Properties of Camelina *methyl Ester (FAMEs) and regular diesel* [86]

Properties	**FAMEs**	**Biofuel Standard ASTM D6751-08**	**Regular Diesel**	**Testing Methods**
Specific gravity	0.88 to 0.90	0.87 to 0.90	0.85	ASTM D287
Viscosity (mm^2/s) at 40°c	4.25 to 4.36	1.9 to 6.0	2.6	ASTM D445
Calorific value (mJ/kg)	39.26	-	42	ASTM D240

Cetane number	47.60 to 48.75	47 min	46	ASTM D613
pour point (°c)	-10 to -8	-15 to 10	-20	ASTM D97

The high amounts of poly unsaturated fatty acids in Camelina oil, causes its weak oxidation stability and the highest potential to form coke during present a drawback for *Camelina sativa* for biodiesel application. Therefore, to make *Camelina sativa* a good row material for use in biofuels it is necessary to reduce the high degree of unsaturation and the molecular weight of the oil [43] and [53]. While, the content of polyunsaturated acids, is the strongest factor influencing the auto-oxidation intensity of fatty acid esters [87].

The heat of combustion (calorific value) measures the energy content in a fuel. The ultimate analysis of a vegetable oil provides the weight percentages of carbon, hydrogen, and oxygen. The higher heating values HHV of vegetable oils ranges from 37.27 to 40.48 mJ/kg. The HHVs of various vegetable oils vary by <9%. The increase in heat content results from a high increase in the number of carbons and hydrogens, as well as an increase in the ratio of these elements relative to oxygen. A decrease in heat content is the result of fewer hydrogen atoms (*i.e.*, greater unsaturation) in the fuel molecule [88], [89] and [1]. Table 2-4, shows calorific value for the types of fuels.

Table 2-4. Calorific value for type of fuels

Type of Fuels	Calorific Value (MJ/kg)	References
Regular diesel	42	[90]
Camelina oil	44.50-46.50	[90]
Camelina biodiesel from TE process by heterogeneous metal oxide catalysts	45.05-46.15	[90]
Camelina biodiesel at supercritical methods	44.97-45.124	[91]
Camelina biodiesel at subcritical methods	45.01-45.18	[91]
Camelina Butyl Ester	39.97	[92]
Camelina Ethyl Ester	39.60	[86]
Camelina Methyl Ester	39.26 45.05-46.15	[86] [46]
Jatropha Methyl Ester	39.65-41.63	[46]
Waste cooking Methyl Ester	39.19	[93]

The calorific values of Jatropha, Camelina, and waste cooking oil esters were lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine [46]. Also, the use of alcohol with longer alkyl chain is favorable to calorific value [86].

For Camelina oil to be better suited for biodiesel, genetic engineering or conventional plant breeding would be required to reduce the high degree of unsaturation and molecular weight. Until that is achieved, however, blending or hydro-treating Camelina oil appear to be alternative strategies for developing it for biodiesel [94].

Pecchia and coworkers reported for the first time a process to improve the Camelina oil quality and its oxidative stability by hydrogenated the methyl esters selectively using a non-toxic and non-pyrophoric heterogeneous copper catalyst (Cu/SiO_2 or Cu/Al_2O_3). This results showed that both catalysts are able to reduce the linolenic acid content below 1% while selectively increasing the monounsaturated one [95].

In general biofuels are prone to more rapid oxidation compared with fossil fuels due to its chemical composition and structure, however, oxidation rate depends on the concentration of natural antioxidants in biofuels and storage conditions (temperature, light, and humidity) [87]. Camelina seeds and raw oil have high concentrations of tocopherol, an anti-oxidant that inhibits rancidity and allows long storage without degradation [79].

Further, life cycle assessments of biodiesel produced from Camelina grown under different conditions showed reduced energy, non-renewable energy inputs and overall greenhouse gas emissions compared to diesel fuel, as well as biodiesel from other oilseed crops, making Camelina more environmental friendly substitute than other biofuel crops [42].

Krohn and Fripp studied the environmental feasibility of Camelina biodiesel and revealed that greenhouse gas (GHG) emissions and fossil fuel use have been reduced up to 40–60% by Camelina biodiesel as compared to petroleum diesel [96]. As well, Camelina biodiesel has been demonstrated to have better performance in decreasing GHG emissions than traditional Soybean*s* and Canola biodiesel [73].

It is important to mentioned that the cold pressed filtered neat oil prepared from Camelina seeds produced greater power output (43.3 kW) compared with (38.5 kW) for mineral diesel fuel [43].

The specific gravity, viscosity, calorific value, and pour point of Camelina oil and biodiesels are going to change with the variation of carbon chains and compositions of biodiesel, for example, Camelina fatty acid methyl esters FAMEs has lower value for each of viscosity (mm^2/s), calorific value (mJ/kg), cetane number and pour point than the Camelina fatty acids, ethyl ester FAEE and butyl ester FABE while has the same specific gravity with FABE which is higher than the FAEE. FABE has higher value of pour point, calorific value and viscosity value. However cetane number has higher value in FAEE [86].

In summary, the reasons behind choosing Camelina as a renewable fuel source are: it can be easily cultivated in anywhere [97], its seeds naturally have high oil content; its oil is low in saturated fatty acids [45]; Camelina is drought resistant and requires less fertilizer and herbicides [82]. In addition to that, the biofuel obtained from Camelina oil meets the requirements of aviation fuel [98], moreover, it has a lower pour point value -11 to -8 than the Waste Methyl Ester -4 to -1, and Jatropha Methyl Ester -6 to +2 according to testing method (ASTM D97) [46].

2.2 Oil Extraction Process

The seed productivity of oil considers as an important process, and agronomists are proceeding to examine ways to enhance the oil output of the seeds as well as ways to domination the composition of the oil [99].

A large range of technologies is available for the extraction of essential oils and active components from plants. The choice based on the economic feasibility and suitability of the process of the specific situation [100].

Nowadays, many of extractive strategies with diversity in terms of methodology, time, temperature, pressure, time and solvents have been developing, also utilized in combination with other techniques to improve the recovery of their extracts. However, due to of the variation between the extractive processes utilized by several companies, there is a diversity in the qualitative and quantitative composition of the extracts resulted from the same plant. Hence, each brand is different in performance and quality of the content of the bioactive compounds [101] and [102].

There are two most important types of processes for obtaining oil: physical and chemical process. The physical process, or expression, involves the use of manual squeezing of ground sample by hand or by mechanical power, such as batch hydraulic pressing and continuous mechanical pressing (screw presses) which also involves hot and cold mechanical pressing, mechanical pressing is the most popular method but less efficient in oil extractability (< 70% oil extraction) [103], [104] and [105].

In other research, the efficiency of seed pressing reached to 80 - 85% [106]. However, it has been generally preferable to follow by a solvent-based extraction, a process by which the oil is separated from the remainder up to 99 - 99.5% [107], [108] and [109]. Mechanical expression results in a good quality oil, but has a relatively low output [110]. Chemical processes (extraction) are depend on solvent extraction. It has an oil extraction efficiency more than 98% [111].

With addition to mechanical expression and solvent extraction there are other methods to use in oil extraction, like supercritical extraction. However, all of these technologies have some advantage and disadvantage; the advantage for mechanical expression and supercritical extraction is output high quality oil, and for supercritical extraction and solvent extraction is produce high yield. while, the disadvantage for mechanical expression is producing a low yield of oil, for solvent extraction is reduced oil and cake quality and for supercritical extraction is requires a huge amount of CO_2 [110]. Classical techniques used for the solvent extraction of natural products are related with longer extraction times, lower product, and utilize of large amounts of organic solvents [112].

To enhanced the efficiency of extraction, some intensification techniques have had to joint with the extraction to improve the yield and quality of extracted products [113] and [99]. An example of an intensification techniques which joined with extraction process are ultrasound [114], microwave [115] and instant controlled pressure drop (DIC) [116] and [117]. Intensification has economic characteristic due to it is considered a secure and valuable method of improving either a rather prolonged (time consuming) or an energy intensive (far from normal conditions) process, looking for the increase of at least one of the essential parameters governing oil extraction process [113].

The worldwide oil seed output will face a growing demand in recent years due to the combination of factors, including a greater consumption for edible oil, the expansion of the biofuel industry, and the requirements for green chemistry [118]. Commonly, there are three different methods for the extraction of oil are conceivable: (1) pressing, (2) solvent extraction, and (3) a combination of pressing and solvent extraction [119].

All extraction processes have three major goals, which are: i/ getting a well performant process in terms of environmental impacts and energy consumption; ii/ getting the extract with a higher yield as possible to be economically efficient; iii/ getting the extract with a higher quality and residue to reach a high economic value of the extraction process [118].

2.2.1 Conventional oil extraction processes

2.2.1.1 Pressing

The mechanical oil extraction or pressing technique for separation of oil from seeds is the most convenient and most economically relevant popular method [120]. However, pressing is less efficient than the solvent extraction, and cannot be easily used to express the oil from seeds with low oil contain such as Soybean*s*; while seeds with higher oil contents are pre-pressed before extraction by solvent [119]. This method offers the possibility of utilizing the meal residue, it also has relatively low initial and operational costs and produces uncontaminated oil [121].

At the laboratory scale, a lot of authors have highlighted the effect of operating parameters (screw rotation speed, temperature, and back pressure) and raw material (seed species, variety, water content and pre-treatment) on process performance (oil yield and press capacity). In general, the main factors influencing the process are the pressure, temperature, and moisture content [108].

Normally, press cake or meal is the by-product of oil processing, but this relationship can change depending on the cost of oil and meal. In addition to the oil, the press cake or meal is a substantial economic factor in oil processing. These by-products can be utilized as a source of protein in animal feeding. In pressing process, it’s necessary to be controlled the oil processing to the necessary quality of the press cake or meal [119].

The principle of this technique is, during the pressing process which seeds are fed in a container and then transported and crushed by a rotating screw in the orientation of a restriction (nozzle). The feeding section of a screw press is loosely filled by seeds material, the initial step of the compression process comprises of rolling, breaking and the displacement and expulsion of air from inter-material voids. When the voids decreased, seeds start to resist the applied force through reciprocal contact. The continuous transport of materials, leaded to increase the pressure to a level necessary to overcome the restriction. This pressure leads to that the oil to be expressed from the seeds [122] and [123].

The continuous movement of material causes pressure to be increased to a level needed to overcome the restriction. This leads to express the oil from the seeds, while the oil is situated at different locations inside the cell, together with other constituents like proteins, globoids and nucleus, all these elements are contained within cell walls, and need to be ruptured to release the oil. A combined force of pressure and friction in the barrel causes the cell walls to rupture and oil to flow out of the liquid solid mixture inside the barrel. The separated oil is discharged through holes available along the press barrel. The press cake or compressed solid material is discharged through the restriction at the end of the barrel [123].

The resistance to alteration in the mechanical behavior of the plant seeds depends on porosity. The higher amount of porosity refers to less resistance to change in the mechanical behavior of the plant seeds with the addition of the lower amount of limit volume energy. It was also obvious that the moisture content of the plant seeds has an effect on volume energy, higher amount of moisture refers to higher resistance to alteration in mechanical behavior of the plant seeds [124].

With a specific target to plan an oilseed press in an ideal way, it is imperative to have a clear insight into the mechanisms of oil expression and an understanding of the important process variables. This can be achieved by modelling the oil recovery from oilseed by using both theoretical and experimental methods. A few examines have been carried out to obtain predictions of oil yield regarding process parameters [125].

Mrema and McNulty modelled the mechanisms of oil expression from C*ashew* and Rapeseed. They reported that there were two main mechanisms involved during oil expression from oilseed. These are the expression of oil from the cells into the intra-kernel voids and final expression of oil out of the seed cake. However, some of the parameters such as the pore radius, number of cell walls, cell wall thickness, are not easily measurable [126].

Mechanical expression process of oil from oilseeds has been successfully characterized by a mathematical model depends on three main equations: the *Hagen Poiseulle* equation for flow of fluids in pipes, to depict the flow of oil through the pores on the cell wall; *Darcy's* law of fluid flow through porous media to depict the flow of oil through the inter-kernel voids; and a modified form of *Terzaghi's* equation for the consolidation of saturated soils, to depict the behavior of the consolidating oilseed meal. The model has been effectively applied to experimental data which detect that the flow of oil crosswise over the cell walls in the seed kernel was the rate determining step [126].

Accordingly the main law governing this flow (q) of fluids through porous media is *Darcy's law* [127]. *Darcy's* empirical flow model represents a simple straight relationship between flow rate and pressure drop in porous media.

$$\mathrm{q}\ (\mathrm{m}^3/\mathrm{s}) = \mathrm{K}\ (\mathrm{dp}/\mathrm{dx}) \qquad \textit{Eq. 2-1}$$

Where: dp/dx is the pressure gradient, K is the coefficient of permeability (m/s) which depends on the porosity of the material [128].

The drawback in this ecological method are low effectiveness of this process and problems with getting a constant quality oil, depending on the quality of crude materials [129].

2.2.1.2 Solvent Extraction

Solvent extraction is the most efficient method of removing the oil from the seed [130]. The choice of appropriate solvent is of primary importance along with application of a suitable extraction method. For choice of solvents *'like dissolves like'* principle is applicable [131].

The fundament of solid-liquid extraction is that when a solid material interacts with a solvent, the soluble components in the solid material move to the solvent by a diffusion process, diffusion can be defined as the process by which the soluble components in the solid material, moving from the relatively high concentration regions into the lower concentration regions. This process can be analyzed in two ways. Initially, it can be described with *Fick's* law and a diffusion coefficient. Second, it can be clarified in terms of a mass transfer coefficient. Thus, dissolvable extraction of plant material outcomes in the mass transfer of soluble active principle to the solvent, and this happens in a concentration gradient. The rate of mass transfer decreases as the concentration of active principle in the solvent increases, till equilibrium is reached. A short time later, there will no mass of the active principle to be transferred from plant material to the solvent. while mass transfer of the active principle also depends on its solubility in the solvent, heating the solvent can increases the mass transfer [100] and [132].

The kinetics of solvent extraction is a function of both the different chemical reactions occurring in the system and the rates of diffusion of the different species that control the chemistry of the extraction process [133]. However, the rate of extraction depends on the thickness and area of solid phase, temperature, solvent and moisture content [134] and [118].

A series of phenomenological steps must occur during the period of interaction between the solid-containing particle and the solvent effectuating the separation, including (1) penetration of the solvent into the solid matrix; (2) solubilization and/or breakdown of components; (3) transport of the solute out of the solid matrix; (4) migration of the extracted solute from the external surface of the solid into the bulk solution; (5) movement of the extract with respect to the solid; and (6) separation and discharge of the extract and solid [135] and [134].

The drawbacks of this method are, this method is not always acceptable for industrial applications because of long extraction time, large consumption of hazardous solvents

[136], with the addition to the prospect of thermal decomposition of the target compounds during the extraction process [137], thus the use of a solvent is not allowed for the output of the extra virgin oil and it is also not beneficial for the production of oil from fruits [138].

It is worth mentioning that this type of extraction can be considered as one of conventional extraction methods which include: soxhlet extraction, maceration, percolation, extraction under reflux and steam distillation, turbo-extraction (high speed mixing) and sonication. Though these techniques are highly used, have several scarcity: are very often time-consuming and require relatively large quantities of polluting solvents, the influence of temperature which can lead to the degradation of thermolabile metabolites [139], [140] and [141].

And unconventional extraction methods include: Ultrasound - Assisted Extraction (UAE), Microwave - Assisted Extraction (MAE), Supercritical Fluid Extraction (SFE), Acceleration Solvent Extraction (ASE), Enzymatic -Assisted Extraction (EAE) and Instant Controlled Pressure Drop (DIC). These all unconventional extraction methods have been developed for the extraction of oil from plants in order to shorten the extraction time, decrease the solvent consumption, increase the extraction yield, and enhance the quality of extracts [99], [142] and [143].

Fundamental studies of solvent reactions performed on vegetable materials (solvent extractions) have demonstrated that the kinetics of these operations are well controlled by the mass diffusivity, this normally leads to weak kinetics and yield. The intensification of such processes almost systematically requires a texturing stage permitting the material to get higher porosity and, then, better diffusivity [133].

To determine which of these techniques are best to use in this research, a review of these techniques will be submitted to identify their limitation.

2.2.2 Innovative Techniques Used to Assist Extraction Process

2.2.2.1 Ultrasound-Assisted Extraction (UAE)

Ultrasound-Assisted Extraction (UAE) includes the use of high-intensity, high-frequency sound waves and their interaction with materials. UAE is a potentially valuable innovation as it does not require complex instruments also it is relatively low-cost [144]. While the mechanism of the extraction includes two types of physical phenomena: diffusion through the cell walls then washing out the cell contents when the walls are broken. It is worth mentioning these both phenomena are significantly affected by ultrasonic radiation [145].

The drawbacks of this technique are; utilized a wide range of solvents or solutions. The extraction is still time-consuming, filtration step needed, repeated extractions may be required [146] and [147].

2.2.2.2 Microwave-Assisted Extraction (MAE)

Microwave is a type of electromagnetic wave whose wavelength range falls in the middle of Radio waves & Infrared waves [148]. The wavelengths ranging from (one meter to one millimeter); with frequencies between 300 megahertz and 300 gigahertz [149].

The principle of microwaves heating depends on the transformation of alternating electromagnetic field energy into thermal energy by influencing the polar molecules of a material. Microwave heating implies that materials can absorb microwave energy directly and internally then change it into heat [150]. Microwaves have magnetic and electric fields which are perpendicular to each other. The electric field causes heating due to two simultaneous mechanisms which named, dipolar rotation and ionic conduction [139]. This method does not require solvent or water and permits the extract (water and essential oils, as well as some non-volatile compounds) to relocate by gravity out of the microwave reactor. The fundamentals of the microwave extraction process happens as the result of changes in the cell structure for the molecules [147].

The drawbacks of this technique are; microwave irradiation can accelerate the chemical reactions or changes of some objective secondary metabolites [151] and [152]. That high microwave power excessively could lead to thermal decomposition of oil to some extent [153] and [154].

Moreover, the extraction efficiency of microwave technique might be very poor when either the target compounds or solvent are nonpolar, or when the viscosity of solvent is considerably high [155] and [99]. In general, microwave assisted extraction is not fit for the extraction of the thermally labile compounds [156].

2.2.2.3 Supercritical Fluid Extraction (SFE)

A supercritical fluid is any material at a temperature and pressure greater than its critical point. It can diffuse through solids like a gas, and dissolve materials like a liquid. There are a large number of compounds that can be utilized as a fluid in supercritical techniques, however by far the most widely utilized is carbon dioxide [157], extraction conditions for supercritical CO_2 are greater than the critical temperature of 31°C and critical pressure of 74 bar, after the extraction, the system solute and CO_2 is compressed and CO_2 is eliminated as a gas [158] and [159].

A supercritical fluid exists in a single fluid phase possessing properties between those of gases and liquids, The critical pressure is the pressure, which causes the gas transformed to a liquid at the critical temperature [160].

The drawbacks of supercritical CO_2 are, because of its non-polar nature, it cannot be utilized for dissolving polar molecules, the solvent power inversely proportional to the molecular weight, Free fatty acids and their glycerides and pigments show low solubility, also water has a low solubility at temperatures below 100^oC, proteins, polysaccharides, sugars and mineral salts are insoluble. Moreover supercritical CO_2 is suitable for separating compounds that are less volatile, have a higher molecular weight and/or are more polar as pressure increases [161], [157] and [162].

2.2.2.4 Acceleration Solvent Extraction (ASE)

Accelerated Solvent Extraction (ASE) or Pressurized solvent extraction (PSE), is a pressurized solvent extraction technique that utilizes solvents at elevated temperatures and pressures to accelerate the chemical extraction process from materials. The higher temperature leads to increase the extraction kinetics, it is also decreasing the viscosity of the liquid solvent and hence enhance diffusivity of the solvent resulting in increased the extraction speed. Whilst, the elevated pressure prevents the solvent from boiling. Furthermore, high pressure forces the solvent into the pores for the solid particles and hence should facilitate extraction of analytes. Researchers proved that there is no evidence was seen for thermal degradation when the extraction of temperature-sensitive compounds by using this extraction technique [139], [163] and [164].

ASE is an efficient way of liquid solvent extraction compared to soxhlet extraction as the method utilize minimal amount of solvent. This extraction technology is able to domination the temperature and pressure for each individual samples and need less than an hour for extraction. Such as other solvent technique, ASE also critically based on the solvent types [165] and [166].

The drawbacks of acceleration solvent extraction are; the equipment used in this technique has very high cost, this extraction is not selective, clean up the extract is usually necessary before the final analysis, at same methods the same sample yield different extract volumes, this perhaps results from perturbation of operation of the static valve, finely the extraction cells consist of 11 pieces, which makes the wash procedure very complicated and causes a significant increase in solvent consumption [167], with the addition to a special attention should be paid to ASE performed at high temperature, which may cause to degradation of thermolabile compounds [100].

2.2.2.5 Enzymatic-Assisted Extraction (EAE)

The enzymes are representing ideal catalysts to assist extraction, synthesis or modification of complex bioactive compounds of natural parent. Various enzymes such as hemicellulase, cellulases, and pectinases are often required to destruct the structural of the plant cell wall entirety, thereby increasing the extraction of bioactive from plants. These enzymes hydrolyze cell wall components thereby enhancing cell wall permeability, which results in increasing extraction yield of bioactive [168], [169], [170] and [171].

The drawbacks of enzymatic-assisted extraction are; the production and isolation of enzymes are expensive relatively, hence enzymes are expensive for huge industrial production, available enzyme is failed to break down the walls of plant cells completely and enzyme assisted extraction is not always proper to be applied in industrial scale because enzymes behave was very limited by environmental conditions [172] and [173].

2.2.2.6 Instant Controlled Pressure Drop (DIC)

The instant controlled pressure drop is a specific a modification of the texturing of the biological product through a rapid expansion of the material without any thermal or chemical degradation [117] and [174].

The definition and first studies of the Instant Controlled Pressure Drop (DIC) process and the thermodynamics of instantaneous transformations were carried out in 1988 [175]. Since that time, DIC technology was utilized and successfully applied at both laboratory and industrial scales in enhancing structure expansion, processing kinetics (drying, extraction of both volatiles and non-volatile compounds, blanching, and sterilization). Usually, DIC has resulted in higher process performance, higher quality of final products in terms of functional and organoleptic properties of natural products and equipment reliability [166], [176], [116], and [177].

Instant controlled pressure drop DIC technology has been initially defined, patented, and developed by *ALLAF* and collaborators, at the University of *La Rochelle*. DIC is a "high temperature (100-170 °c), high steam pressure (0.1–0.7mpa)-short time (usually between 5 and 60 s)" treatment followed by an abrupt pressure drop towards vacuum [178], [179] and [116].

The pressure drop induces a whole swelling of the product with a possible controlled destruction of cell walls. This well-controlled modification of the texture of the material intensifies functional behavior and technological efficiency [180].

DIC is a high-temperature/short-time process. It involves in the first stage charging the material in the treatment vessel, heating it usually up to 160 °C using high-pressure (up to 0.8 MPa) of saturated steam, for a short period of time (some seconds or dozens of seconds). Once the equilibrium at both temperature and water content within the product is attained, the second main stage is performed inferring an abrupt pressure-drop whose rate $\Delta P/\Delta t$ is higher than 0.5 MPa s^{-1}, towards a vacuum (usually at 5 kPa). Figure 2-2, shows schematic time-temperatures-pressures profiles of a DIC processing cycle. DIC is distinguished from other treatment techniques by a pressure-drop rate higher than 0.5 MPa/s which cause an expansion and rapid cooling of the product [179].

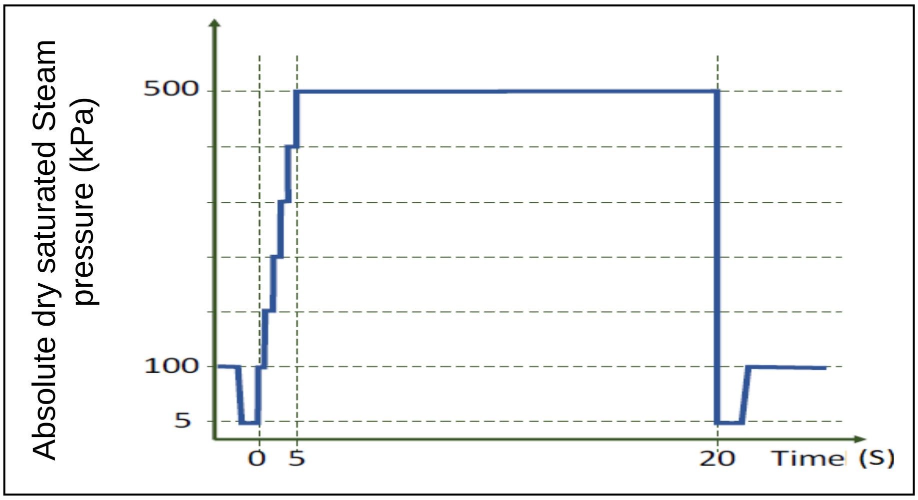


Figure 2-2. Schematic time- pressures profiles of a DIC processing cycle, including 1/ establishment of the vacuum within the processing reactor; 2/ injection of dry saturated steam at the selected pressure level; 3/ maintain of treatment pressure during selected time; 4/ instant controlled pressure drop towards a vacuum and 5/ establishment of the atmospheric pressure within the processing reactor

The fundamental of DIC is; the high temperature of the process is generated by subjecting the raw material for a short period of time to high pressure saturated steam. The abrupt pressure-drop generates an auto-vaporization of volatile molecules, which denote instant cooling of the sample, and allows the structure to be further expanded [143].

Furthermore, products treated with DIC usually have a shelf life of more than two years, and that due to DIC usually maintains product color, taste, and vitamins; it also effect on the increasing the decontaminates the raw materials and gets rid of insects [179]. In addition, through texturing, DIC involves a decrease in the cost of performance, due to decrease energy consumption by reducing the operating time [176]. DIC has permitted solvent extraction to be carried out very efficiently with a more effective washing step and higher diffusivity in a shorter time using less solvent [143].

The general applications of the DIC–process according to the invention pertain are; pasteurization, debacterization, and sterilization, preparation of vegetables or fruits so as to facilitate their peeling and/ or their pressing, modification of the structure of the treated materials, separation of treated materials components, enhance the quality of the finished product or extract, growing the value of the by-products or reducing the technical steps of the operations, etc. this invention pertains to the precise control of these treatments by means of governing the temperature and the period of thermal, hydrothermal, thermomechanical and hydro thermomechanical treatments. Therefore, the present invention in its general form pertains to a process for the treatment of solid products, particularly of biological products in piece, powder or paste form, also miscible or non-miscible liquid products [174].

2.3 Biodiesel

During the last century, the consumption of energy has highly increased due to the change in the lifestyle and the significant growth of population. This increase in energy request has been supplied by the utilize of fossil resources [181], which caused; the scarcity of conventional petroleum (fossil) fuels, growing emissions of combustion-generated pollutants, and their expanding costs, will make biomass sources more attractive [1].

This expanding demand for energy has led to looking for alternative sources of energy that would be socially equitable, economically efficient, and environmentally sound [181].

To meet the rising energy demand and replace fossil fuel reserves, fuels like biodiesel and bioethanol are at the forefront of alternative technologies [1], there is a need to develop convenient long-term strategies based on usage of renewable and environmentally friendly fuels that would gradually substitute the dropped production of fossil fuel due to the exhaustion of the world‘s accessible oil reservoirs [182]. Accordingly, the viable alternative for compression-ignition engines is selected to be biodiesel [1].

Biodiesel defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as, animal fats or vegetable oils [183], provide a clean and effective fuel for diesel engines. This makes them attractive for employ as additives in petroleum based diesel fuels [184].

Thus biodiesel is distinguished than diesel fuel in terms of aromatic content, sulfur content, flash point and biodegradability [1].

In the most general term, biodiesel refers to any diesel fuel substitute derived from renewable biomass. More selectively, biodiesel is defined as an oxygenated, sulfur-free, non-toxic, biodegradable, and eco-friendly alternative diesel oil, and also it should to meet the special requirements such as the ASTM and the European standards [181].

Biodiesel is miscible with petrodiesel in all proportions, this has led to the use of blends from biodiesel with petrodiesel rather than neat biodiesel. Often blends with petrodiesel are denoted by acronyms such as B20, which indicates a blend of 80% petrodiesel with 20% biodiesel [30], this proportional is frequently used in the United States this proportion of blending provides an correct balance between material compatibility, performance, cold weather operability, and emission benefits [185]. Furthermore, because the energy content of petroleum and biomass oil fuel~~s~~ are close enough, that is lead to minimize the fuels economy issues with blends up to 20% [186]. However, biodiesel also can be utilize as a fuel in its neat form (B100) if suitable precautions are taken [185].

Animal fats and vegetable oils are originally water-insoluble, hydrophobic substances in the plant and animal world that are constituent of three moles of fatty acids and one mole of glycerol and are commonly referred to as triglycerides (TAGs) [187].

Chemically, TAG are esters contain several different fatty acids (FA), these different fatty acid are attached to one glycerol backbone. Because different fatty acids have different chemical and physical properties, the fatty acids profile is the most important parameter affect the corresponding properties of an animal fat or vegetable [30].

The large molecular size of the triglycerides result in the oil having higher viscosity (10 times larger than that of diesel oil), lower the reactivity of unsaturated hydrocarbon chains and volatility compared with that of petroleum diesel, leads to occur problems directly after prolonged use of the vegetable oils in engines, particularly with direct-injection engines. These problems include: fuel atomization does not occur properly or is even prevented as a consequence of plugged orifices; carbon deposits on the injectors; oil ring sticking and thickening, finally gelling of the lubricating oil as a consequence of contamination by the vegetable oils, so it is necessary to subject the vegetable oils to treatments that reduce the viscosity [181], [182], [188] and [187].

The usefulness of vegetable oils as diesel fuel include: liquid nature-portability; have heat content up to 80% of diesel fuel); easy availability and renewability [182]. Vegetable oil combustion has cleaner emission [181], it has the potential to minimize the level of pollutants and the level of potential carcinogens [187]. Also, these fuels are readily biodegradable, they have a practically null sulfur content, and no problems probable during their transport and storage [188].

2.3.1 Characteristics of Oils and Fats Used in Biodiesel Production

Fats and oils are commonly indicated to as triacylglycerol (triglycerides) because the glycerol molecule consists of three hydroxyl groups where a fatty acid can be attached. All triacylglycerol own the same glycerol unit, thus it is the fatty acids which contribute the different properties. The fatty acid components are featured in three ways: (i) chain length, (ii) the number and position of the double bonds,-(iii) the position of the fatty acids within the glycerol molecule [54].

The ASTM specification for biodiesel allows for a variety of feedstocks and processes to be utilized in its production [185]. Both the chemical and physical characteristics of fats and oils are affected greatly by the types and proportions of the component fatty acids and the way in which these are attached to the glycerol molecule [189].

Biodiesel properties also depend on the fatty acid composition of the oils raw materials because the fatty acid profile of biodiesel is corresponding to that of the original oil. In turn, the properties of fatty acid esters (FAEs) are specified by the chemical structure of the fatty acids (FAs); the most significant features are the degree of unsaturation and the chain length [85].

Fatty acid esters have physical properties nearer to fossil diesel fuels than pure vegetable oils [190]. For example, the pour point and cloud point temperatures, iodine index, and cetane number depend on the number of unsaturation and the length of the fatty acid chains. A greater content of double-covalent bonds gives a higher iodine index and a lower solidification point [15].

In general, unsaturation fatty acids has a negative relationship with each of; viscosity, high calorific value, cetane number, filterability limit and cloud point, oxidation stability and specific heat, while has a positive relationship with flash point. However, chain length of fatty acids has a negative relationship with filterability limit and cloud point, and positive relationship with the others physical properties with the exception of oxidation stability which there is no relation or effect between it and chain length. Finally, the fatty acids with branching structures has a negative relationship just with cetane number and positive relationship with viscosity, and there are no relationship between it and each of high calorific value, flash point, oxidation stability and filterability limit and cloud point [191].

However, there are other chemical parameters influence the physical properties, such as, the relation between presences of aromatic compounds and cetane number, the greater the number of aromatic compounds, cause the lower the cetane number, also the position of the double bonds has an effect on cetane number, the closer the double bond is to the end, lead to a greater cetane number will be [191]**.**

in a research done by Geller and Goodrum [184]; they observed a notable difference between FAMEs mixtures obtained from vegetable oils and FAMEs derived from pure fatty acids to be; that the FAMEs mixtures based on vegetable oil consistently showed better performance as lubricity enhancing additives than did FAMEs mixtures based on single fatty acid with addition to that the vegetable oil-based FAMEs have an additional factor affecting lubricity which is not active in pure FAMEs [184].

2.3.2 Physical Transformations

2.3.2.1 Direct Use of Oil and Blending

Since in 1980, there was considerable discussion regarding the use of vegetable oil as a fuel. Bartholomew illustrated the concept of utilizing food for fuel, revealing that petroleum should be the alternative fuel combustion.

The direct use of vegetable oils in the diesel engine is not compatible and cause to problems because it has many inherent failings, where polyunsaturated fatty acids were very capable of polymerization and gum formation due to oxidation during storage or by thermal polymerization at the higher temperature and pressure of the combustion [192].

Although the vegetable oils have familiar properties as biodiesel fuel, it is still required to some chemical modifications before it can be used in the engine. Energy consumption with utilize of pure vegetable oils was found to be identical to that of diesel fuel. For short-term use, proportion of 1:10 to 2:10 oil to diesel has been found to be effective [193] and [194].

Since the high viscosity of the oil is the main obstacle to use it directly in the engines. Also, the viscosity controlled the suitable ratio for oil blending with petroleum, for example; Canola oil is more viscous than the other commonly tested vegetable oils and, according to the viscosity is temperature-dependent, at 10°C, the viscosity of Canola oil and diesel fuel were to be 100 and 4 cSt respectively, thus the viscosity of the 75:25 blend of Canola oil and diesel fuel determined to be 40 cSt. Also, the viscosity can be lowered by blending the oil with pure ethanol, for example, at 37°C, the viscosity of blend of Canola oil with10% ethanol was to be 21.15 cSt, while that of pure Canola oil at this temperature was 37.82 cSt [187] and [195].

2.3.2.2 Micro-Emulsion of Oils

Micro-emulsion is defined as a as a colloidal equilibrium dispersion system of water, oil and an amphiphile which is optically isotropic and thermodynamically stable liquid solution. Researches have been proceeded on reducing high viscosities of vegetable oils by producing micro-emulsions with short chain immiscible alcohols, such as methanol, ethanol, and 1-butanol. Micro-emulsion with these solvents has met the maximum level of viscosity needed for diesel fuel. however, micro-emulsion of vegetable oil decrease their viscosity but has been found to produce in irregular sticking of injector needle with the addition to heavy carbon deposits due to oil incomplete combustions [26] and [29].

2.4 Chemical Transformation

2.4.1 Pyrolysis of Biomass

Pyrolysis is the thermal decomposition of the materials in the absence of oxygen or when the quantity of the oxygen for complete the combustion is lower than required. Pyrolysis is the essential thermochemical process for converting biomass into a more valuable fuel [1].

Pyrolysis of biomass is the heating of solid biomass in an absence of oxygen to produce; gaseous products mainly such as; H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6 and benzene, liquid bio-oil products such as; high molecular hydrocarbons, tars and water, liquid product may closely like either gasoline or petrodiesel depending on reaction conditions such as; heating rate, final reaction temperature, residence time, carrier gas flow rate and presence of catalyst, and solid products (char). it is possible to modify the proportions of the gas, liquid and solid product by changing the final temperature and the rate of heating [196] and [30]. Figure 2-3 shows the mechanism of thermal decomposition of triglycerides.

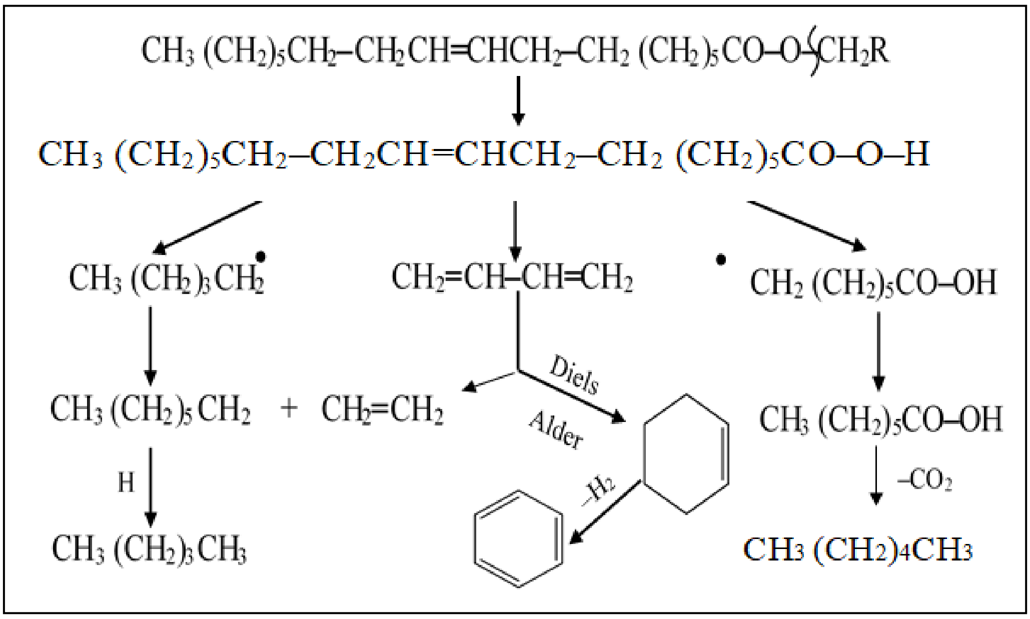


Figure 2-3. The mechanism of thermal decomposition of triglycerides [182]

2.4.2 Biodiesel Production Process

Theoretically, vegetable oils and waste oils can be used as a fuel directly [197]. *Jones and Peterson* in their literature concerning using vegetable oils as a replacement for diesel fuel, concluded that the short-term engine testing reveals that vegetable oils can easily be utilized as a fuel source when the vegetable oils are utilized purely or are blended with diesel fuel. However, long-term engine durability studies displayed that fueling diesel engines with pure vegetable oil causes engine failure [198].

Since engines were designed to burn diesel fuel, therefore this engines may not operate properly with vegetable oils which have ~~a~~ high viscous and low volatile properties. So there are four major methods used to minimize the high viscosity of vegetable oils: These are direct use or blending of oils with petrodiesel, pyrolysis, micro-emulsification and transesterification. Due to the quality of the fuel produced, the transesterification is the most preferred methods to produce fuel from different feedstock types, only the transesterification process leads to the products commonly known as biodiesel, (alkyl esters of oils and fats) [199], [31] and [30].

Transesterification is the chemical reaction which converts a vegetable oil or animal fat to biodiesel [200], [201], [32] and [202]. Biodiesel produced by this reaction has identical properties to conventional petroleum diesel [203] and [197], Therefore, the researchers has been concentrated on chemically changing the vegetable oils to biodiesel, also there is the potential to carry out this reaction directly inside the oleaginous structure. This in-situ transesterification (ISTE) process effectively results in more convenient industrial process [204], [205], [206] and [34].

It is worth to mention, there are two types of renewable diesel fuels; green diesel and biodiesel. The difference between them is that, the biodiesel is primarily made by esterification process, while the renewable diesel made by catalytic hydroprocessing of the same triglyceride feedstocks applied to produce biodiesel. In hydroprocessing process, alkanes be produced which are chemically corresponding to some of the compounds found in petroleum diesel fuel, alcohol is not required, and glycerol byproduct is not formed [207] and [185].

2.5 Transesterification of Vegetables Oils

Transesterification, is the general expression used to describe the significant class of organic reactions where an ester is transformed to another by an interchange of the alkoxy charge. The transesterification process is also called alcoholysis [32].

This reaction process consists of two-step, in the first step, lipids are extracted from the biomass using a solvent or mechanical methods, and then in the second step the refined lipids are converted to fatty acid methyl ester using alcohol and catalyst [208] and [209]. Transesterification is the reaction of a fat or oil with an alcohol to produced esters and glycerol [210]. The reaction is shown in Figure 2-4.

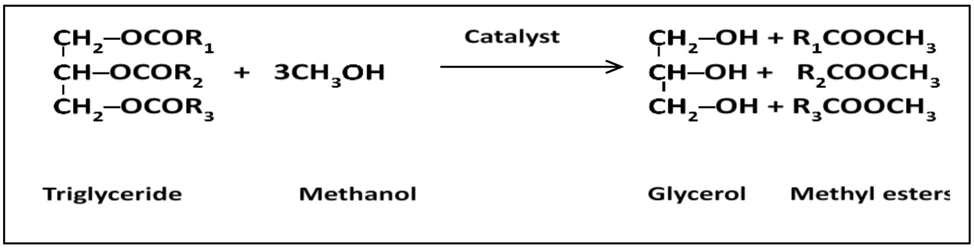


Figure 2-4. General equation for transesterification of triglycerides [208]

The main reason that animal fats and vegetable oils are transesterified to alkyl esters (biodiesel) is that the biodiesel kinematic viscosity is frequently closer to that of petrodiesel. The high viscosity of un-transesterified fats and oils has resulted in operational problems in the diesel engine such as deposits on different engine parts. While there are engines that can use un-transesterified oils, the greater majority of engines require the lower viscosity fuel [30].

However, it has been noted that biodiesel yield was reduced during conventional transesterification due to the existence of gums and extraneous material in the crude vegetable oil, thus refining and purification of extracted oil become very important stages prior transesterification [211].

The reaction is reversible, and thus an abundance of alcohol is usually needed to force the equilibrium to the product side. The stoichiometry of the reaction is (3:1) alcohol to lipids (oils). However, in practice this is usually expanded to (6:1) in order to raise the product yield [212].

This reversible reaction and the yield of biodiesel highly depend on the properties of reactants (such as; purity and structure) and the type of catalysts utilized. whereas the original property of catalyst would be the determining factor in the choice of a suitable reactor [213] and [214]

However, the process conditions must be neatly controlled to achieve optimal yield [8].The main factors affecting the transesterification reactions are; the molar ratio of glycerides to alcohol, type and the ratio of catalyst, reaction temperature and pressure, time of reactions, and the contents of free fatty acids and water in the oils [33].

In general, alcohols that can be used in biodiesel production are those with short chains including; methanol to pentanol alcohol [15].

In general, the most prepared esters are methyl esters, because methanol is the minimum costly alcohol, although there are exceptions in some countries. for example, In Brazil, where ethanol is less expensive, ethyl esters are utilized as fuel [30]. Ethanol based biodiesel does not create as much thermal energy like methanol-based biodiesel. The distinction in energy output has to do with the concentration levels of the alcohols and the molecular structure [215].

According to *Camelina sativa* fatty acid esters, the saturated degree decreases with the increase of the alkyl chain of the alcohols from methanol, ethanol, to butanol [86].

In a comparative study of direct transesterification of *Camelina* oil under supercritical methanol, ethanol and 1-butanol conditions, the researchers found that the transesterifications time of these three supercritical alcohols with *Camelina sativa* oil required to reach the equilibrium is rising with the increase of the length of the carbon chain of alcohols. Also, they revealed that the physical properties of *Camelina sativa* biodiesels and regular petroleum diesel fuels are comparable. The cold properties, calorific value, and cetane number of biodiesel are enhanced with the increase of the length of the carbon chain of alcohols, while these properties are inversely proportioned to the unsaturated degree in biodiesels compositions [86].

Moreover, transesterification process also required some catalyst to increase the rate of the reaction and quality of the outcome product. The quantity and type of catalyst are selected by the amount of free fatty acid exist in the raw oil. The higher quantity of free fatty acid is undesirable for biodiesel production which leads to produce of soap and lower the efficiency of biodiesel yield [210] and [216]. The catalysts can be alkalis, acids, or enzymes [182].

Recently, *Yang et al.* conducted a comparative study on the alkaline catalysts transesterification optimization of unrefined *Camelina* oil using response surface methodology. The optimal conditions of *Camelina* transesterification were 33.6°C as reaction temperature, 6.9:1 as molar ratio of methanol/oil, and 1.66% as catalyst concentrations. The optimized biodiesel yield was 95.6% wt [67].

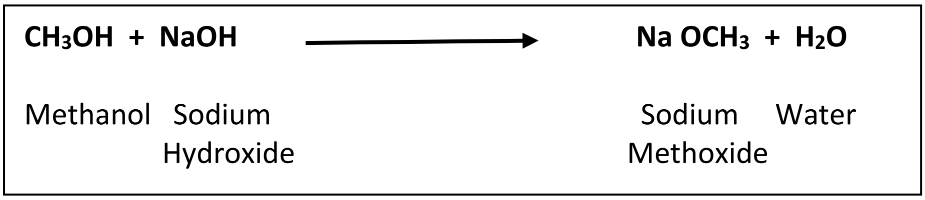
Transesterification process can be classified according to the type of catalyst which used in this process, such as; Alkali or Base Catalyzed Transesterification, Acid-Catalyzed Transesterification Enzyme-Catalyzed Transesterification and Heterogeneous Catalysts [182] and [217].

2.5.1 Alkali or Base Catalyzed Transesterification

The most technique often used for industrial production of biodiesel is a transesterification reaction with homogeneous base-catalyzed [209] such as, sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), sodium ethoxide ($NaOCH_2CH_3$), potassium hydroxide (KOH), and potassium methoxide ($KOCH_3$). These type of catalyst are commonly utilized because of several advantages like; economically available, able to catalyze reaction at low reaction temperature and atmospheric pressure, and high conversion in shorter time [218], [209], [219] and [220].

When catalyst concentration is increased, the biodiesel yield increased. However, the biodiesel yield is decreased when the basic catalysts are added above their optimum concentration due to soap formation [219].

In general, homogeneous alkaline preferred to use as a catalyst in transesterification reaction when the feedstocks oil has a low concentration of free fatty acids and water to avoid side product formation and subsequent low yield [221]. This type of catalyst form water when dissolved in the alcohol reactant [220]. This reaction is shown in Figure 2-5 [222].

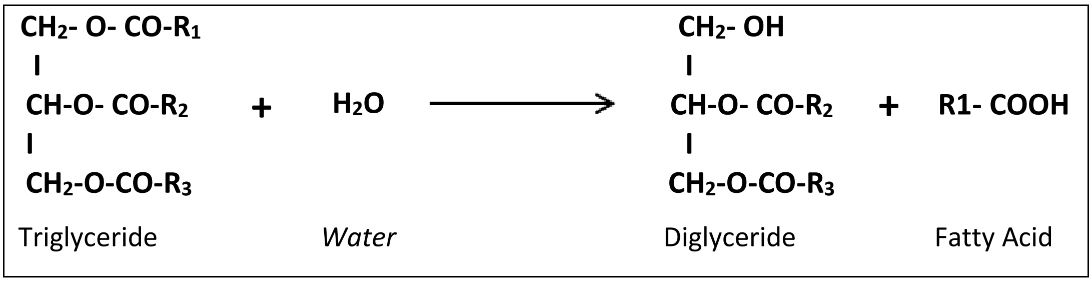


$$\underset{\text{Methanol}}{\mathbf{CH_3OH}} + \underset{\substack{\text{Sodium}\\\text{Hydroxide}}}{\mathbf{NaOH}} \longrightarrow \underset{\substack{\text{Sodium}\\\text{Methoxide}}}{\mathbf{Na\,OCH_3}} + \underset{\text{Water}}{\mathbf{H_2O}}$$

Figure 2-5. Undesirable reactions of NaOH in triglyceride transesterification reactions

However, water has huge negative consequences for this kind of transesterification process [223].

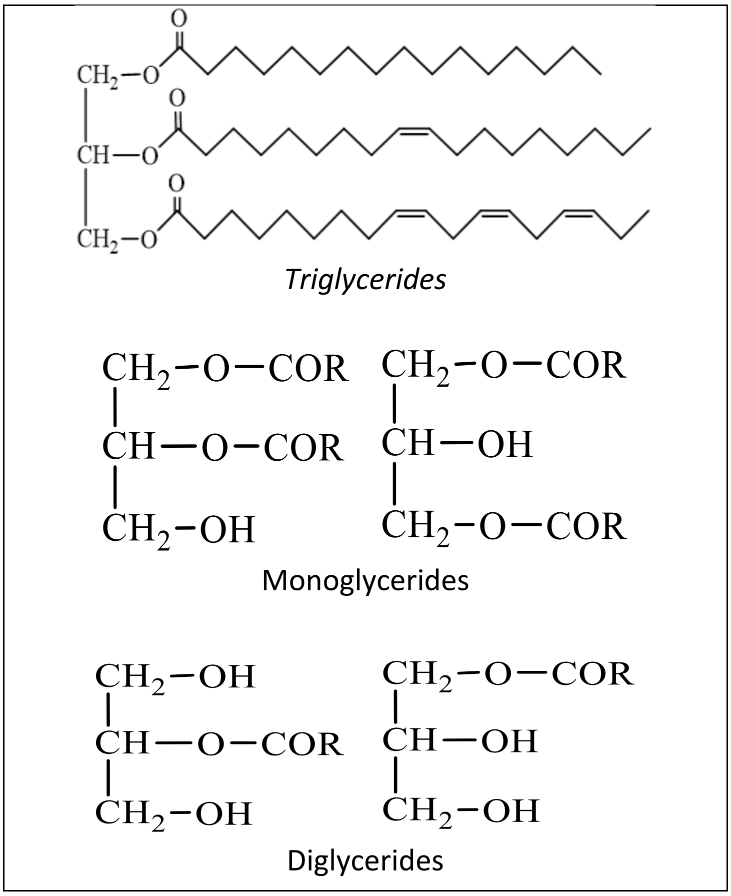
In particular, water can accelerate the hydrolysis of esters, basically the triglycerides, which produces free fatty acids (FFA). Then the FFA formed partially consume the homogeneous alkaline catalyst, which leading to the production of soaps and producing more water [224] and [225]. This vicious circle results to a very low reaction transformation and biodiesel yield [209]. The typical hydrolysis reaction is shown in Figure 2-6 [220].



$$\begin{array}{lcccccl} CH_2\text{-}O\text{-}CO\text{-}R_1 & & & & CH_2\text{-}OH & & \\ | & & & & | & & \\ CH\text{-}O\text{-}CO\text{-}R_2 & + & H_2O & \longrightarrow & CH\text{-}O\text{-}CO\text{-}R_2 & + & R1\text{-}COOH \\ | & & & & | & & \\ CH_2\text{-}O\text{-}CO\text{-}R_3 & & & & CH_2\text{-}O\text{-}CO\text{-}R_3 & & \\ \text{Triglyceride} & & \textit{Water} & & \text{Diglyceride} & & \text{Fatty Acid} \end{array}$$

Figure 2-6. The typical hydrolysis reaction

Moreover, the saponification reaction also happens between the catalyst and glycerin esters (triglycerides, diglycerides, monoglycerides and FAMEs); Figure 2-7 [209].



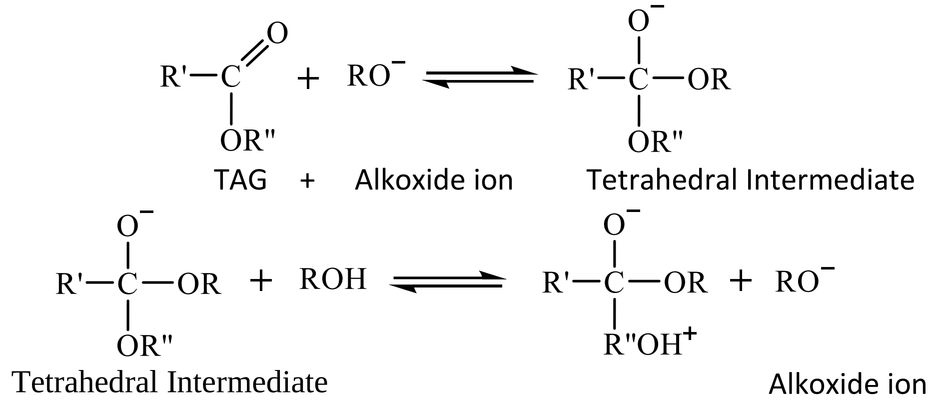
R_1-COOH (FFA) + NaOH (Sodium Hydroxide) ⟶ R_1COONa (Soap) + H_2O

Figure 2-7. Chemical formula of glycerin esters

This reaction is unfavorable because the soap reducing the yield of the biodiesel and difficulties the separation of the esters from the glycerol. In addition, it associated with the catalyst meaning that more catalyst will be required and then the process will include a higher cost. The saponification reaction of the homogeneous alkali catalyst (sodium hydroxide) and the FFA, forming soap and water is shown as below [220] and [217].

In the alkaline homogeneous transesterification process it is recommended that the FFA content of the raw oil ~~to~~ should be less than 0.5-1 wt. % [226] and water content in the oil should be removed before to transesterification [227] and [221]. In order to diminish the effects of FFA and water on the homogeneous base catalyzed transesterification, the pretreatment to dehydrate and deacidify the raw materials have been vastly applied in industry to ensure the water concentration of the oil feedstock is a <0.06 wt. % and an acid value <1 mg KOH/g. However, such pretreatments unavoidably lead to an expansion in energy consumption and operating cost [228].

The advantages of the utilized base catalyzed transesterification reaction, are it’s roughly 4000 times faster than acid catalyzed transesterification. While the disadvantages are, glycerides and alcohol should be considerably anhydrous, else it leads to saponification, which diminishes the catalytic efficiency, forms gels and leads to difficulty in separation of glycerol and the molar ratio of methanol to oil has to be 6:1 or higher rather than the stoichiometric 3:1 proportion [229]. Figure 2-8, illustrate the mechanism for transesterification by homogeneous base catalysis.



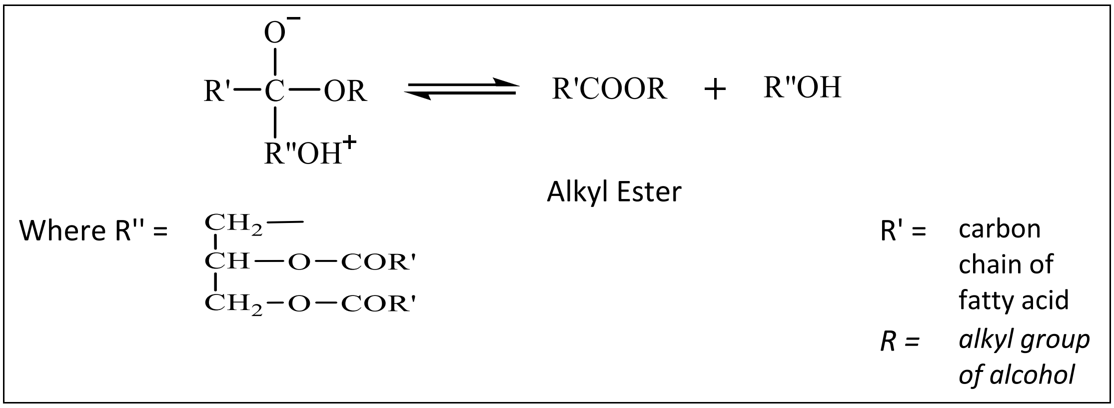


Figure 2-8. Mechanism for homogeneous base catalysis in transesterification

2.5.2 Acid- Catalyzed Transesterification

When the oil or fat contains significant amounts of FFA (>5%), then another type of catalyst will be required to use in transesterification reaction instead of using the base material as a catalyst which always causes big problems. For these cases, an acid catalyst such as sulfuric acid can be utilized to esterify the FFA to methyl esters [30].

Acid catalysts can be used to catalyze both esterification and transesterification through its ability to avoid saponification formation and FFA is directly transformed to ester through esterification process, while glycerides are transformed to ester through transesterification whereas base catalysts only catalyze transesterification but not esterification [230]. Mechanism of esterification showed in Figure 2-9 [220].

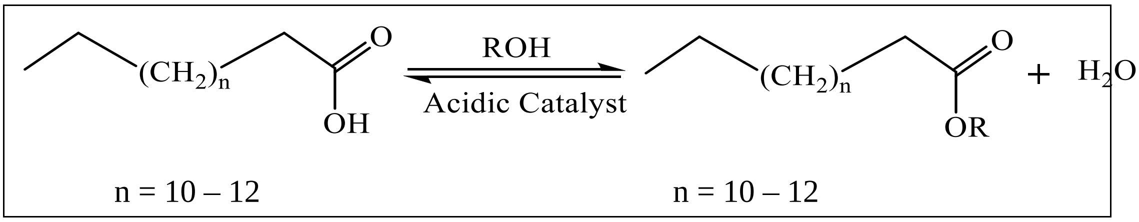


Figure 2-9. Esterification reaction of fatty acids for biodiesel production

As mentioned before that during the alkali transesterification reaction, water is accumulated as a by-product which inhibits the reaction if not removed, while acid catalysts have the ability of to produce FAMEs from both FFA and acyl-glycerol offers sufficient advantages that this type of catalyst was shown to be superior to alkali catalyst or to combine acid/alkaline catalysis in an economic biodiesel production from [30].

The mechanism of esterification and transesterification reactions by acid- catalyzed is shown in Figure 2-10. The first step is protonation of the carbonyl group in the glyceride molecule which results to carbocation. Then the attack of alcohol generates a tetrahedral intermediate. The removal of glycerol backbone from this intermediate leads to the production of the esters [230].

The comparison between acid and alkali-catalyzed transesterification detect that acid catalyzed has, longer reaction times, due to slower rate of the reaction, higher reaction temperatures, and higher cost materials of construction are required to obtain satisfying yield [30] and [230].

Acids utilized for transesterification include sulfuric, phosphoric, hydrochloric, Boron trifluoride and Trifluoroacetic acid. Sulfuric acid is the favored acid for this reaction, due to it is the most economical acids, also and by the investigated done on a series of Bronsted acids revealed that only this acid has the efficiency to achieve high conversions in the transesterification of Soy oil with methanol. It has a perfect catalytic activity and easily in H_2SO_4/ MeOH preparation as concentrated liquid. The most prevalent H_2SO_4 concentration utilize in esterification is (1–2%) [201], [230], [231] and [30].

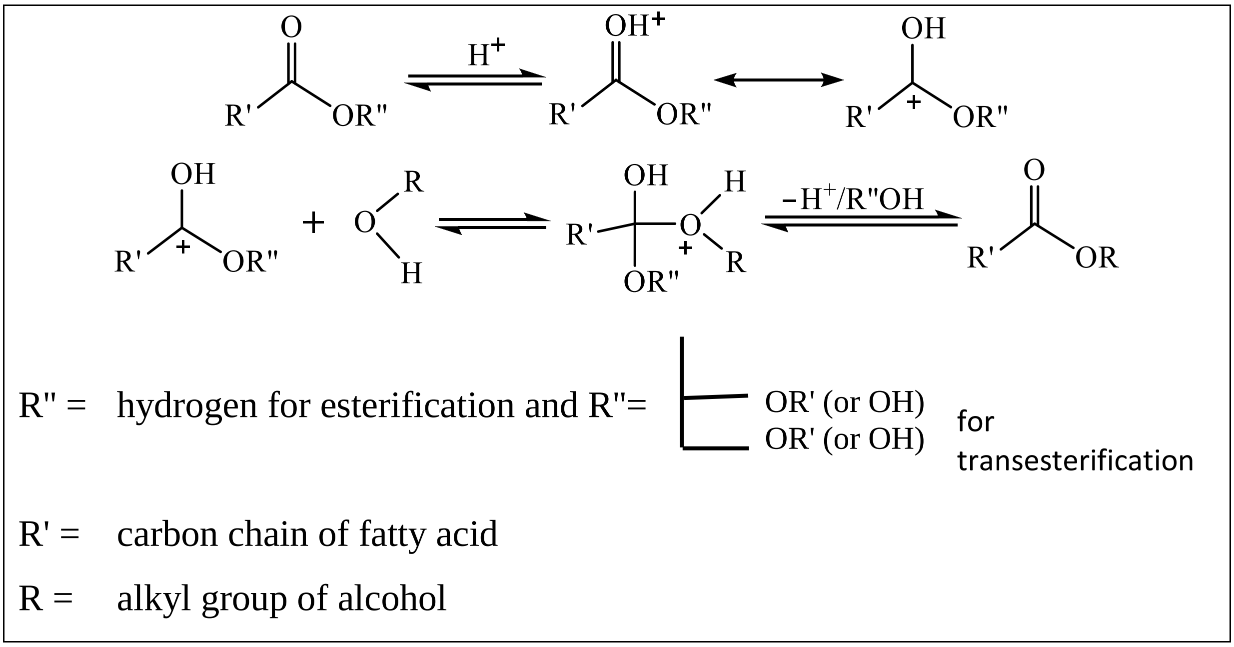


Figure 2-10. Mechanism for homogeneous acid catalysis in esterification and transesterification [230]

The most investigators reported a great level of conversion to methyl esters when using utilizing acid catalysts. *Harrington* and *D'arcy-Evans* accomplished the 98% conversion of Sunflower seed oil to FAMEs utilizing a methanol/sulfuric acid mixture [232] and [233].

2.5.3 Heterogeneous Catalysts

Heterogeneous catalysts can be alkali such as; (CaO, $CaZrO_3$, $CaTiO_3$, CaO-CeO_2, $Ca_2Fe_2O_5$, $CaMnO_3$, KOH/Al_2O_3, Al_2O_3/KI, ETS-10 zeolite, alumina/silica supported K_2CO_3), or acids such as; (ZrO_2 /$SO^{-2}{}_4$, ZnO/I_2, TiO_2/$SO^{-2}{}_4$, carbohydrate-derived catalyst, carbon-based solid acid catalyst, vanadyl phosphate, niobic acid, sulfated zirconia, Amberlyst-15, Nafion-NR50) [220].

The heterogeneous catalyst in transesterification reaction is distinguished from the homogeneous catalyst that it has the higher tolerance towards FFA’s in the oils, easier to separate from the product, and reusable catalyst. However, the heterogeneous process has also been noted to suffer from mass transfer restrictions between liquid and solid phases, and the activity of the solid catalyst can be adversely affected by the existence of water in the oils/fat [221] and [234].

Figure 2-11 shows a comparison between homogeneous and heterogeneously catalyzed transesterification. Some heterogeneous catalysts are solid and it could be easily separated from the product by filtration, which decreasing the washing requirement. Furthermore, solid heterogeneous catalysts can catalyze both of the transesterification and esterification reaction, thus these catalysts are especially useful for those feedstocks with high free fatty acid content [220].

In heterogeneous catalysis, water acts as an inhibitor of the catalyst, but influences neither the ester yield nor the glycerol purity [221].

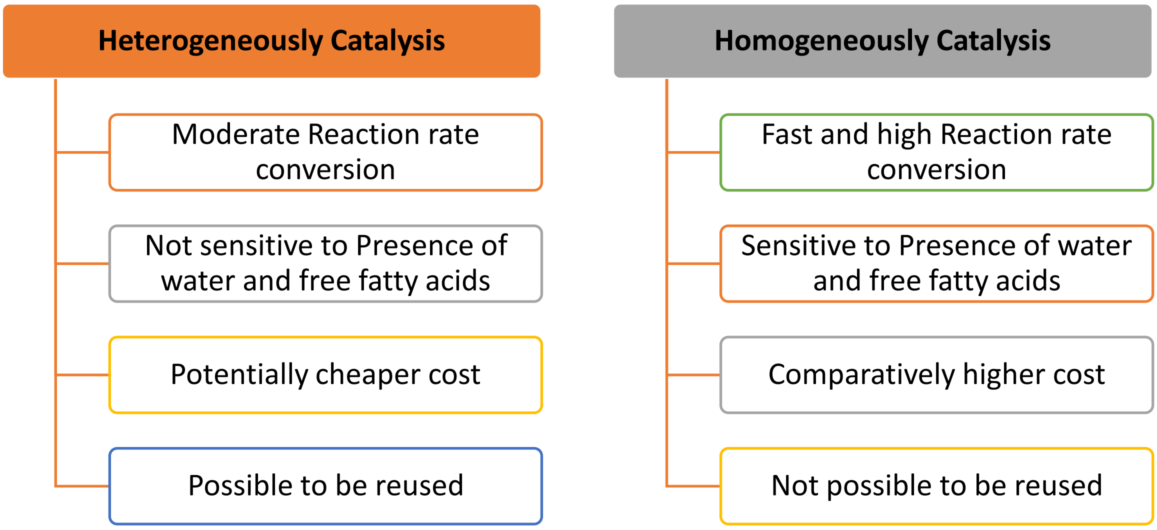


Figure 2-11. Comparison between homogeneous and heterogeneously catalyzed transesterification [229]

2.5.4 Enzymatic -- Catalyzed Transesterification

Enzymes are biological catalysts and have enormous potential for decreasing energy requirements and environmental issues in the chemicals pharmaceutical industries [14].

Recently, enzyme catalysts have become more attractive because it is can avoid soap formation and the purification process is easy to achieve. Also, with an advantage is that no purification is fundamental for utilizing these biocatalysts [220].

It is also reported that the enzymatic transesterification, is a less energy intensive than the other methods and has other advantages like; simple glycerol recovery, complete conversion of FFAs to methyl esters, and no requirement for waste water treatment [221].

However, Enzymatic transesterification is less regularly utilized commercially due to the longer reaction times, higher cost [220] and higher catalyst concentration is needed to completion of reaction, although repeated utilize of lipase becomes possible after immobilization of lipase on transporter, it loses its activity in 100 days of application [14] and [235].

Furthermore, the enzyme catalysts in transesterification reaction often is required a solvent to avoid deactivation of the enzyme by un-dissolved alcohol [221].

Finally, Transesterification process commonly utilize pre-extracted oil as raw material, which is usually produced by mechanical pressing followed by solvent extraction to extract the residual oil. Alternatively, biodiesel can be produced by in-situ transesterification (reactive extraction). This process merges the steps of lipid (oil) extraction and transesterification to output biodiesel [236].

2.6 *In-situ* Transesterification

In transesterification process, the oil extraction and transesterification proceedings are carried out separately for the conventional biodiesel production [35], although the transesterification process is not energy consuming and the transformation capacity is good [237], but this operation is recognized as expensive due to the numerous steps required [238], which can lead to a long time requirement and use different operating units [35].

On the other hands, the *in-situ* transesterification process had been distinguished from transesterification process, by that the feedstocks reacting with alkalized or acidified alcohol directly instead of reacting with pre-extracted oil and alcohol. That is, extraction and transesterification proceed occurred in one step. That is mean in this process the alcohol acting as an extraction solvent and an esterification reagent [34]. To minimize the alcohol requirement for better efficiency during in-situ transesterification, the oilseeds required to be dried before the reaction occurs [220].

This biodiesel production method could help in the facilitation of the fuel conversion process, due to removing the solvent extraction step, potentially lowering the overall process cost, also minimize the long size of the production system which associated with the pre-extraction steps, degumming, and enhance the yield of the biodiesel production, hence reducing the final fuel product costs. However, this process cannot use animal fats and waste cooking oils, which can minimize the cost of feedstock [239], [240], [220], [241] and [242].

Theoretically, transesterification reaction needs three moles of alcohol for each mole of oil. In the process of reactive extraction or in-situ transesterification with either an acid or alkaline catalyst, molar ratio of alcohol to seeds is considerably greater than the value calculated depend on the stoichiometry of the transesterification reaction.

hence, extra methanol will be needed due to its act as an extraction solvent as well as a reactant [243] and [244]. The outputs from the conventional process (transesterification) are; crude methyl ester, glycerol, and alcohol. Whereas the outputs for in-situ transesterification process include the same of conventional outputs in addition to the residual solid material from the seeds (cake). The existence of the solid materials in in-situ transesterification makes the purification step distinct from that in conventional processes, as a filtering process to separate the cake from other products is necessary. while the other steps of both processes are similar such as, methanol recycling process, water washing and separation of methyl ester from the other products due to gravitational settlement [238].

Figure 2-12 show the comparison between transesterification and *in-situ* transesterification process.

In a research to investigate the variables affecting the *in-situ* transesterification process done on microalgae lipids, *Ehimen, Sun,* and *Carrington* indicates that the increasing in the temperature and the reacting alcohol volume leads to enhance fatty acid methyl ester (FAMEs) conversions. With the exception of *in-situ* transesterification did at room temperature (23°C), the equilibrium FAMEs conversions seem to approach asymptotic limits for reaction times more than 8 h for all temperatures researched. Stirring the reaction vessel affected the rate of biodiesel formation. Finally, Increasing the moisture content of the microalgae biomass had a powerful negative influence on the equilibrium FAMEs yield, and *in-situ* transesterification process was inhibited when the biomass water content was more than 115% w/w (in view of oil weight) [245].

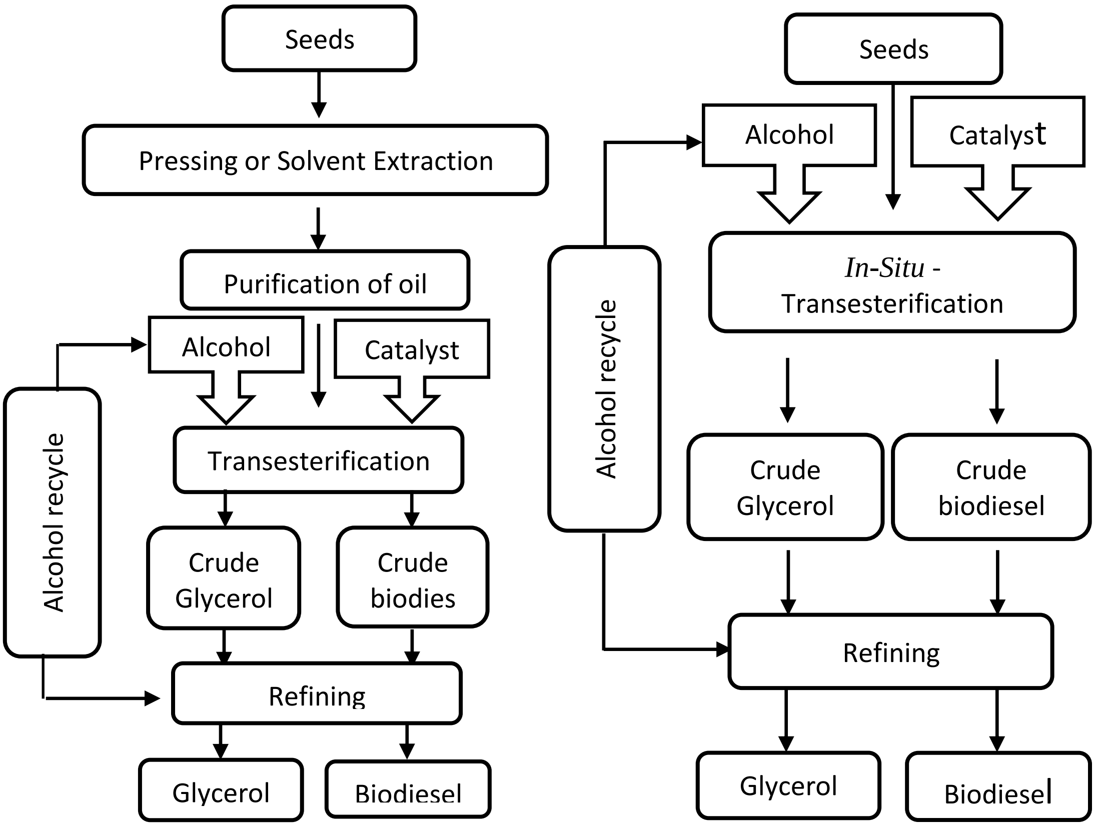


Figure 2-12. Comparison between transesterification and in-situ *transesterification process*

In another research done by *Harrington and D'arcy-Evans*, to compare between the percentages of FAMEs yield from transesterification and *in-situ* transesterification from *S*unflowers, they investigate that under reflux conditions Sunflower seeds were transesterified with an abundance of methanol in respect to the number of moles of triacylglycerol (TAG) present utilizing sulfuric acid as catalyst, they observed ester formation with yield over 20% greater in the in-situ transesterification than in the transesterification of pre-extracted oil. They ascribed this behavior to an impact of the water content of the seeds, to an enhanced extractability of some seed lipids with acidic conditions, and to the transesterification of seed-hull lipids [246]and [243].

To reveal if in-situ transesterification is appropriate to all lipid-bearing materials, in an experiment performed on (meat/bone meal) and (distillers dried grains with soluble). Both types of raw material comprise low percentages of oil, but the oil fractions of (meat/bone meal) and (distillers dried grains with soluble) were successfully transformed to methyl ester at rates of 91% and 93% respectively [247] and [238]. It's worth to mention in this process acidic catalyst is more favorable to use for *in-situ* transesterification of vegetables' oil seeds [243].

Due to the biomass feedstock is used directly in the *in-situ* method that is lead to reduce the time required to obtain biodiesel. The single-step process can be incorporated with other technology such as microwave irradiation and instant controlled pressure drop (DIC) to improve biodiesel productivity [35] and [248]. As mentioned before the DIC technique is an intensification method used with both extraction steps in transesterification reaction and with *in-situ* transesterification reaction, due to DIC procedure provided structural modification in terms of expansion, higher porosity and improvement of specific surface area; which leads to increase the diffusion of solvent inside the seeds [249].

In this study, the focus will be on this technique to produce biodiesel from seeds, then make a comparison between the biodiesel quantitatively and qualitatively before and after using the DIC technique to improve the economic viability of the industrial section of produced biodiesel.

CHAPTER 3. EXPERIMENTAL PART - MATERIALS AND METHODS

3.1 Raw material

The biodiesel feedstock was natural dried (sun-dried) *Camelina sativa* seeds harvested from France fields (*Sanctum Mediterranean*). Ethanol 95%, glacial acetic acid (100%), methanol 99.9%, toluene 98% and n-Hexane (HPLC grade 99.9%) were purchased from Merck, sulfuric acid 99% from Sigma-Aldrich, and anhydrous sodium phosphate, as well as Isopropanol, potassium hydroxide, phenolphthalein indicator, iodine, bromine water, potassium iodide, starch indicator, and sodium thiosulfate were purchased from Alpha.

3.2 Response Surface Methodology (RSM)

Response surface methodology is a collection of mathematical and statistical techniques valuable for developing, enhancing, and optimizing products and processes. The most comprehensive applications of RSM are especially in situations where numerous input variables have a possible impact on some performance measures or quality characteristics of the process or product. RSM start from a design of experiments (DoE) to determine the factors (independent variables) values for conducting experiments and collecting information. The information is then used to develop an empirical model that relates the process response to the factors [250] and [251]. The most common applications of RSM are in clinical, industrial, social Food, biological, physical and engineering sciences [252].

The goal of utilizing RSM is to develop procedures that would bring a better understanding of the combined impacts of the key processing variables on the desired responses to accomplish the best mathematical system performance of statistical previsions. RSM is typically utilized after performing an adequate Design of Experiments (DoE) choosing operating parameters and their own particular extents. This is regularly based on collecting data from literature, initial experience, and exploratory experiments [253], [254] and [255].

However, the major objectives of RSM is the determination of the optimum settings of the control variables that result in a maximum or a minimum response. This requires possessing a ‘good’ fitting model that gives an adequate representation of the mean response in order such a model is to be used to determine the value of the optimum. Optimization techniques utilized in RSM depend on the nature of the fitted model [256] and [252].

A good fit to the experimental data is usually achieved based on the following RSM results: (I) the standard deviation of the proposed mathematical model is low. (II) the parameters of a model should be significant, else they will not contribute to the model; it is considered excellent if the regression coefficient (R^2) is up to 90%, also it is considered good if the regression coefficient is up to 70%, while; the mathematical model is not good fit if the regression coefficient is less than 70%. (III) The value of the objective function has to be low. (IV) The proposed mathematical model should be statistically significant [254].

In general, the structure of the relationship between the independent variables and the response is unknown. The first step in DoE is to get a proper approximation close to the true relationship. The more common forms are low-order polynomials (first-order Eq. 3-1 or second-order Eq. 3-2) [257].

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n-1} \sum_{j=2}^{n} \beta_{ij} \chi_i \chi_j \qquad \textit{Eq. 3-1}$$

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij} \chi_i \chi_j \qquad \textit{Eq. 3-2}$$

Where:

Y is the response or dependent variable: χ_i and χ_j are the independent variables; β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively estimated by the model.

The second-order model is utilized over the first-order model in response surface methodology for some reasons, for example, the second-order model is very flexible.

It can take on a vast variety of functional forms, thus it will predominately work well as an approximation to the true response surface. Also, it is simple to estimate the parameters (the β's) in the second-order model. The method of least squares can be utilized for this purpose and there is significant practical experience revealing that second-order models work well in solving real response surface problems [258].

Thus; the second-order polynomial empirical model was proposed for the Response Surface Modeling (RSM in these studies. Statgraphics for Windows software (5.1 version), SIGMA PLUS Neuilly sur Seine, France for designing experiments and statistically treating the responses was used. RSM was separately used as optimization procedures for each of extraction, transesterification and *in-situ* transesterification processes.

3.3 Treatment Methods

3.3.1 Main Treatments of Camelina Seeds

Oil extraction by pressing and/or solvent ways.

3.3.2 Intensification of Oil Extraction through Texturing of Camelina Seeds by Instant Control Pressure Drop (DIC) Treatment

Fundamental studies of solvent extractions and/or solvent reactions performed on vegetal materials have demonstrated that the kinetics of such operations are well controlled by the mass diffusivity [99]. This normally results in weak kinetics and yield. The intensification of such processes almost systematically requires a texturing stage allowing the material to get higher porosity and then greater diffusivity. The instant controlled pressure drop is a specific texturing way able to take place in different materials without necessary involving any thermal or chemical degradation [117].

Texturing treatment was carried out on Camelina seeds raw material using DIC technique. The oil extracted from the DIC-treated seeds, was transesterified to biodiesel. The DIC treated seeds were *in-situ* transesterified to biodiesel. The same conversion processes (conventional and *in-situ* transesterification) were carried out on raw Camelina seeds for comparison purposes.

The treatment vessel where the sample of the material is placed and treated usually is double-jacket chamber. The vacuum system is composed of a vacuum tank with a volume 130 times greater than the processing vessel, and a suitable vacuum pump. The initial vacuum level was preserve at 50 kPa in all the experiments. The pneumatic valve (3) assures the connection/separation between the vacuum tank and the processing vessel. It can be opened in less than 0.1 s; this ensures the abrupt pressure-drop within the treatment vessel. *Figure 3-1* shows the schematic diagram of DIC unit.

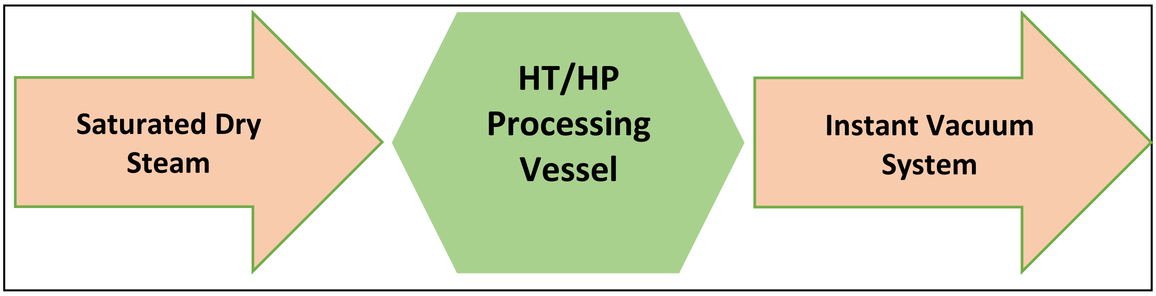


Figure 3-1. Schematic diagram of DIC unit

3.3.3 Design of Experiment DoE for DIC Treatments

In order to reduce the experimental trials required to identify the effect of the main operating parameters (steam temperature T and processing time t), a 2-component rotary design of experiment was developed with 13 experiments including 2^2=4 factorial points, 2*2=4 star points and 5 replicates for the central point. The experiments were run randomly to minimize the effects of unexpected variability due to unusual responses. Table 3-1 and

Table 3-2 list the independent variables, actual and coded levels.

Table 3-1. The factorial design matrix with the coded levels of the independent variables

	Processing temperature ˚C	Processing time (s)
Point min (-α)	115	15
Point (-1):	122.3	19.4
Central point	140	30
Point (+1):	157.7	40.6
Point max (+α)	165	45
Value of 1	17.7	10.6

Table 3-2. Actual values of the independent variables for DIC

Sample	Processing temperature °C	Processing pressure (MPa)	Processing time (s)
DIC1	140.0	0.36	30.0
DIC2	165.0	0.7	30.0
DIC3	140.0	0.36	45.0
DIC4	140.0	0.36	30.0
DIC5	157.7	0.58	40.6
DIC6	157.7	0.58	19.4
DIC7	140.0	0.36	30.0
DIC8	122.3	0.21	19.4
DIC9	122.3	0.21	40.6
DIC10	140.0	0.36	30.0
DIC11	115.0	0.17	30.0
DIC12	140.0	0.36	15.0
DIC13	140.0	0.36	30.0

α (axial distance) = $\sqrt[4]{N}$

Where: N = number of experiments of orthogonal design. In this case there are 2 parameters, so: α= 1.4142.

The surface responses were obtained by using the analysis design procedure of statgraphics for windows software (5.1 version, SIGMA PLUS Neuilly/Seine, France) for designing experiments and statistically treating the responses. According to the experimental design 13 samples from Camelina seeds were treated by DIC at different temperature and time.

3.4 Extraction of Oil from *Camelina Sativa*.

Oil is extracted from the seeds by various processes such as, maceration, distillation, cold pressing, solvent extraction or supercritical CO_2 extraction [53]. Each method possess its advantages and disadvantages [259]. Agronomists still investigate ways to improve the oil output of the seeds while controlling its composition [260]. The choice between this wide range of technologies depends on the economic feasibility and suitability of the process to the particular situation [261]. Commonly, Camelina oil is extracted from the seeds by pressing and solvent extraction and the preferable solvent is hexane [53] and [117].

3.4.1 Mechanical Pressing

To obtain the oil of *Camelina sativa* by pressing, a screw press type *Skeppsta Maskin AB (Oil press Tàby Presse Type 40 A,* Sweden) Figure 3-2, was used. The capacity of the press is approximately 8 - 16 kg seeds/ hour. The restricted size of the press cake outlet can be varied by placing different sized nozzles (with *Camelina s.* seeds nozzle size 7 mm) get better results. To prevent jamming the press head is heated to 70-80˚C using a hot iron ring. While continuing heating 200 g from each Camelina (14 pattern, 1 from raw material and 13 from DIC treatments), were placed in a cylindrical container, then were subjected to the pressure load. Crude oil is collected at the oil outlet and the press cake exit on the left in the shape of small wire. The amount of oil collected was considered as the weight of oil extracted Figure 3-3. After pressing a sample of the press cake was analyzed on oil content with solvent extraction. Table 4-2. Oil yield from mechanical pressing yield, shows the percentage of oil produced by mechanical pressing.

Figure 3-2. Persse Type 40 A, (Sweden)

Figure 3-3. Camelina oil collected from pressing

3.4.2 Solvent Extraction of Oil from Camelina Seeds and Pressing Cake

Oil extraction was performed for Camelina seeds (14 samples) and the corresponding cakes produced as by-products from pressing process, (14 samples), using reflux apparatus Figure 3-4. The solvent extraction protocol was as the following:

10 g of Camelina cake or 5g of Camelina grinding seeds; which were pre-ground by (coffee grinder *CLATRONIC*, Germany) was weighed into a round bottom flask, then 130 ml of n-Hexane was then charged into the round flask.

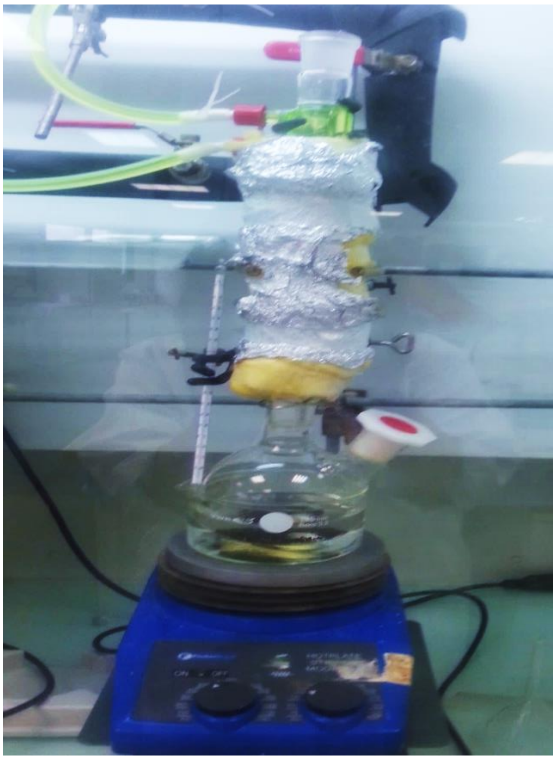


Figure 3-4. Camelina seeds solvent extraction

A condenser was connected to the flask. The set up was held up with a clamp and is mounted on the heating mantle. The condenser was connected to a water reservoir and water flows constantly through the condenser and heating mantle were switched on at 60 ± 2 ºC. Extraction time selected to be 2 hours, after which heating process is stopped. The mixture of oil and solvent is kept to cool. In order to separate the oil from solvent, rotary evaporator (*BUCHI* R-215, Swiss) was used. The reminder oil was weighted to calculate the percentage of oil yield.

In general, the oil extraction operating conditions are: ratio of seeds/solvent 1:26 (w/v), heating temperature 60 ± 2 ºC, extraction time for 2 hours, and 600 rpm agitation speed. Table 4-3 and Table 4-5 shows the percentage of oil extracted from the seeds and the cakes.

3.5 Assessment Methods

3.5.1 Measurement of Moisture Content of Un-textured and DIC-textured Seeds

Camelina sativa seeds were sun-dried (natural drying). The water content of the samples was measured by the Infrared halogen technology (*OHAUS MB45 Moisture Analyzer,* Switzerland), Figure 3-5. The initial moisture content of the dried *Camelina s.* seeds has been determined to be 0.0420 g H_2O/g db.

Figure 3-5. OHAUS MB45 Moisture Analyzer

The moisture content of *Camelina s*. seed after DIC treatment for all the experiments was measured by two methods, oven and IR moisture analyzer.

Oven-dry method uses weight loss to obtain a direct measure of the moisture content of the samples. Specific weight of each sample was placed in an aluminum pan and was dried for 24 hours under an air flux at 105°C. Samples were after that cooled, weighed then the moisture content was calculated. It is worth noting that the safe moisture content for storage of seeds decreases with increase in oil content [262].

The IR moisture analyzer method involves heating the samples by absorption of IR radiation, the loss in weight measured during drying represents the moisture content of the samples [263]. Table 4-1 shows a comparison between the moisture content values obtained from oven and IR moisture analyzer.

Oven-dry method is the most accurate and adopted by various standards (AATCC, AFNOR, etc. methods) of determining the moisture content of seeds at any moisture content [264]. The moisture content of the seeds can be expressed by two ways, the first one called the "moisture content on oven dry basis, it's the ratio of the amount of water in a seed compared to the oven-dry weight of seeds.

$$\%\ \text{Moisture content} = \frac{(\text{orginal weight} - \text{oven dry weight})}{(\text{oven dry weight})} \qquad \textit{Eq. 3-3}$$

The second one called the "moisture content on oven wet basis, it's the ratio of the amount of water in a seeds compared to the original weight of seeds [265].

$$\%\ \text{Moisture content} = \frac{(\text{orginal weight} - \text{oven dry weight})}{(\text{orginal weight})} \qquad \textit{Eq. 3-4}$$

3.5.2 Determination of the Oil Physicochemical Properties

3.5.2.1 Determination of oil extraction Yield

The percentage yield of oil is the quantity of oil extracted in a specific time relative to the weight of the *Camelina s.* seeds used.

$$\text{yield}\ (\%\ \text{wb}) = \frac{\text{Weight of oil extract}}{\text{Weight of seed sample}} \qquad \textit{Eq. 3-5}$$

3.5.2.2 Determination of Oil Density [266]

The empty dry density bottle (*pycnometer*) was weighed and the weight was recorded. The dry density bottle was filled with the oil sample; the pycnometer as well as capillary hole in the stopper is filled with oil.

The spare oil that leaks through the capillary hole was dried with a filter paper and total weight was then measured. The density measurements are carried out at 25°C.

$$\text{Density of oil} = \frac{\text{Weight of oil}}{\text{Volume of oil in pycnometer}} \qquad \textit{Eq. 3-6}$$

3.5.2.3 Determination of Kinematic Viscosity of Oil [267]

Kinematic viscosity is a measure of the time for a fix volume of liquid to flow by gravity through a capillary. The unit of kinematic viscosity is stoke which is expressed as cm^2/s or 10^{-4} m^2 s-1, also there is centistoke unit, and the relation between the two units is:

$$\mathrm{St} = \mathrm{cm}^2 s^{-1}; \mathrm{St} = 100\ \mathrm{cSt}; 1\ \mathrm{cSt} = 1\ \mathrm{mm}^2 s^{-1} \qquad \textit{Eq. 3-7}$$

A viscometer (Viscometer, *Cannon Fenske Routine*, Eurostar Scientific LTD, PSL ASTM-IP 100, UK) was placed in a thermostatic water bath maintained at the 40 °C. The charged viscometer was allowed to remain in the bath long enough to reach the test temperature, transfer the sample to another viscometer arm by gentle suction until the meniscus of the sample rises to the specific area then allowed the sample to flow to a reset state. The flow time of oil samples was recorded with a stopwatch (ravencourt). The kinematic viscosity (ν) was calculated using the formula:

$$\nu = \mathrm{kt} \qquad \textit{Eq. 3-8}$$

Where:

k is the Viscometer constant (mm^2 s^{-2})

t is the test time (s).

3.5.2.4 Determination of Oil Refractive Index [268]

Refractive index has been measured according to ASTM D1218, using Refractometer (*Bellingham and stanley Ltd*. Abbe 60/95 refractometer, UK), Figure 3-6. The measurements were carried out at 25°C.

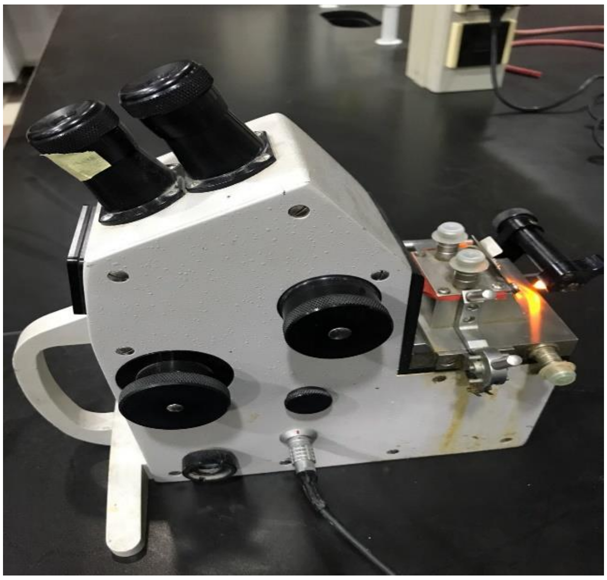


Figure 3-6. Abbe 60 refractometer

3.5.2.5 Determination of Oil Peroxide Value [269] ***and*** [270]

30 ml of the acetic acid chloroform solution was charged into a flask containing 2g of the oil sample. Then a 0.5ml saturated solution of potassium iodide was added, followed by the addition of 30 ml of distilled water. Then the flask mixture was titrated against 0.1M sodium thiosulphate until the yellow color disappeared. 0.5ml starch indicator was added and the titration continued until the end point (where the blue color just disappeared). A blank titration was also performed. The peroxide value was calculated using the following formula:

$$\mathrm{PV} = \frac{(\mathrm{S} - \mathrm{B}) \times \ \mathrm{N\ thiosulfate}\ \times 1000}{\mathrm{Weight\ of\ sample}} \qquad \textit{Eq. 3-9}$$

Where:

PV =Peroxide value as milliequivalents peroxide per 1000 g sample.

S = titration of sample volume.

B= titration of blank volume.

N = normality of $Na_2S_2O_3$ solution.

3.5.2.6 Determination of Oil Acid Value [271]

5 g of the oil sample was taken in a dry conical flask and dissolved in 50 ml of absolute ethanol, then 3 drops of phenolphthalein were added. The flask was heated and

shaken in water bath for 10 minutes, then cooled. Then the sample was titrate against 0.1 N KOH until the pink color appears (end point). The acid value is calculated by using the following equation:

$$\mathrm{AV} = \frac{\text{Titration value } \times \mathrm{N} \times 56.1}{\text{Weight of sample}} \qquad \textit{Eq. 3-10}$$

Where:

56.1 = KOH molecular weight g/mol

N= KOH normality.

3.5.2.7 Determination of Oil Free Fatty Acids (FFA) [271] ***and*** [272]

During decomposition of glycerides in oil free fatty acids are formed. The FFA value is the number of milligrams of KOH required to neutralize 1g of the oil. The percentage of free fatty acids in most types of fats and oils are calculated as oleic acid, although in coconut and Palm kernel oils it is frequently expressed as lauric acid and in Palm oil in terms of palmitic acid. Acid value can be converted to FFA (expressed as oleic acid) by the following formula:

$$\%\mathrm{FFA} = \frac{\text{Titration value } \times \mathrm{N} \times 28.2}{\text{Weight of sample}} \qquad \textit{Eq. 3-11}$$

Where:

N = Normality of KOH

28.2 = oleic acid molecular weight in mg/mol

Acid value and FFA% are correlated as the following:

$$\mathrm{AV}/56.1 \ = \ (\mathrm{v} \ - \ \mathrm{b}) \ \mathrm{x}\, \mathrm{N} \ / \ \mathrm{w} \qquad \textit{Eq. 3-12}$$

And

$$\mathrm{FFA\%}/28.2 \ = \ (\mathrm{v} \ - \ \mathrm{b}) \ \mathrm{x}\, \mathrm{N} \ / \ \mathrm{w} \qquad \textit{Eq. 3-13}$$

The percentage of free fatty acid is commonly calculated in expression of oleic acid, 1000 g of sample contains 282 g of oleic acid. Combining Eq. 3-12 and Eq. 3-13 resulted in:

$$\mathrm{AV}/56.1 = \mathrm{FFA\%} / 28.2 \qquad \text{Eq. 3-14}$$

Or

$$\mathrm{AV} = 1.99\mathrm{FFA\%} \qquad \text{Eq. 3-15}$$

$$\mathrm{FFA\%} = 0.503\mathrm{AV} \qquad \text{Eq. 3-16}$$

3.5.2.8 Determination of Oil Saponification Value [273]

25 ml of the ethanolic potassium hydroxide solution was charged into a round bottom flask contain 2.0 g of oil sample. The flask was attached to a reflux condenser, the solution was boils gently until the sample is completely saponified (homogeneity and clarity of the test solution are partial indicators of the complete saponification). This usually needed to approximately 1 hour, 7 ml phenolphthalein solution was added and the mixture was titrated against 0.5M Hydrochloric acid solution until the pink color disappeared. A blank titration was also carried out. The saponification value was calculated using the following equation:

$$\mathrm{SV} = \frac{\mathrm{B} \times \mathrm{S} \times \mathrm{M} \times \mathrm{M.wt}}{\text{Weight of sample}} \qquad \text{Eq. 3-17}$$

Where:

B = blank titer value

S = sample titer value

M= Molarity of Hydrochloric acid

M.wt. = Molecular weight of Hydrochloric acid

3.5.2.9 Determination of Oil Ester Value and Percentage of Glycerol [266]***,*** [274]***,*** [275] ***and*** [276]

The ester value is the number of milligrams of potassium hydroxide (KOH) required to saponify the esters in 1 g of sample. Ester value is the difference between the saponification value and the acid value

$$\text{Ester value} = \text{Saponification Value} - \text{Acid Value} \qquad \textit{Eq. 3-18}$$

If glyceride is present, the difference between acid number and saponification number is a rough measure of the glycerol present. The following empirical equation is used to estimate glycerol content:

$$\%\ \text{Glycerin} = (92 \times 100\ \times \text{Ester value})/(168\ \times 1000) \qquad \textit{Eq. 3-19}$$

Where:

168 mg of KOH generates 92 mg of glycerol; thus, the above equation could be presented in another expression:

$$\%\ \text{Glycerin} = 0.0546\ \text{Ester value} \qquad \textit{Eq. 3-20}$$

3.5.2.10 Determination of Oil Iodine Value [277]

Iodine value is expressed as the degree of unsaturation of oils and fats. 0.25g of the sample oil was dissolved in a 500 ml flask by 10 ml of carbon chloroform and 30 ml Hanus solution. The mixture was left for 30 minutes with continuous shaking. Then 10 ml of 15% potassium iodide was added, then followed by 100 ml distilled water. The mixture was titrated with standard 0.1M sodium thiosulphate ($Na_2S_2O_3$) solution while shaking well till the pink color disappearing on adding starch. A blank titration was also carried. Iodine value was calculated using the following equation:

$$\text{Iodine value} = \frac{\text{B} - \text{S} \times 0.1 \times 12.69}{\text{Weight of sample}} \qquad \textit{Eq. 3-21}$$

Where:

12.69 = each milliliter of sodium thiosulfate solution is equivalent to 12.69 mg of available iodine.

B = blank titration volume.

S = sample titration volume.

3.5.3 Fatty Acid Profiles by GC Chromatography

FAs analysis were performed using an (*GC 2010 Shimadzu*, Japan, gas chromatograph); Figure 3-7, equipped with flame ionization detector, and a Capillary Column SP 2380 (30 m, 0.25 mm, 0.20 µm) poly (90% biscyanopropyl/10% cyanopropylphenyl siloxane). Nitrogen was used as the carrier gas at injector volume 1 µL, injector temp. 250 °C, detector temp. 270 °C and oven temp. 150 – 230 °C (4°C/min).

Figure 3-7. Shemadzo Gas Chromatography

FAMEs were identified and the fatty acid profile of Camelina oil was determined by comparing the retention time of the peaks eluted from the sample chromatogram with standard peak values, allocating the peaks accordingly and quantifying the amounts versus the standard FAMEs mixture. Before undergoing gas chromatography analysis, the oil had to be converted into the ester form, to reduce its boiling point, also because gas chromatography GC–FID is over 13 times more sensitive to fatty acid methyl esters (FAMEs) than either tri-acyl glycerides (TAG) or free fatty acids (FFA), also FAMEs behave more ideally in GC analyses at lower temperatures than their parent species. The eluted peaks then were compared to those of the individual fatty acid methyl ester standards [238], [278], and [279]. In the present work, Camelina oil was converted to FAMEs by transesterification process using optimum conditions which have been described in below:

3.6 Biodiesel Production

3.6.1 Transesterification Process (TE)

In the current work, a comparative study has been conducted on Camelina oil using the acid catalyst transesterification and *in-situ* transesterification process which normally preferred acid catalyst than alkaline catalyst [280] and [281]. TE was conducted to the oil produced from pressing fresh raw Camelina seeds, and oil produced from pressing of the DIC-textured Camelina seeds. The processes for biodiesel production have been modeled and optimized using response surface methodology.

The transesterification processes were conducted in a laboratory-scale setup; solvent type (Methanol: Toluene (90:10), reaction temperature of 60˚C, agitation speed 600 rpm, and reaction time of 2 h, catalyst type H_2SO_4, were applied based on literature data [282].

With the objective to identify the optimum conditions for high yield (Y) of Fatty Acid Methyl Esters FAMEs, the impact of experimental parameters; the ratio of solvent to raw Camelina seeds oil; solvent/ oil (S), reaction time (t) and acid catalyst concentration (C), have been investigated. Preliminary experiments allowed us to identify the ranges of solvent/oil ratio from 3:1 to 17:1 v/v, time from 0.5 to 7 h and catalyst/solvent ratio from 1% to 10 % v/v.

Each trial started by preparing a reactive mixture with adequate amounts of both solutions of methanol/toluene and acid catalyst in a 500-mL round bottom flask with reflux condenser. This mixture was then placed in the magnetic stirrer hot plate (LabT Ech, Korea), shaken at 600 rpm until the catalyst was completely dissolved, and at the same time, pre-heated to the desired reaction temperature 60 °C.

Simultaneously, 5 ml of Camelina seeds oil, separately, was placed in a beaker and heated to 60 ˚C for 10 minutes. When the methanolic /catalytic solution had reached the desired temperature, Camelina oil which heated to 60 ˚C was introduced into the solvent-catalyst solution. The main step of the reaction was achieved by keeping temperature at 60˚C and mechanical mixing at constant speed 600 rpm for 2 hr. Figure 3-8 show the final product from TE process.

Figure 3-8. Final product from TE

Afterwards, the mixture was left for 24 hours in a separator funnel Figure 3-9 A to allow separation of glycerol from the ester phase Figure 3-9 B. After separation, the crude biodiesel was washed 3-4 times with warm distilled water followed by 0.1 % Sodium Hydroxide to remove trace amounts of catalyst in the methyl ester Figure 3-9 C. The washing was repeated until a clear water layer of neutral pH was obtained. The washed biodiesel Figure 3-9 D was first dried using anhydrous sodium sulfate.

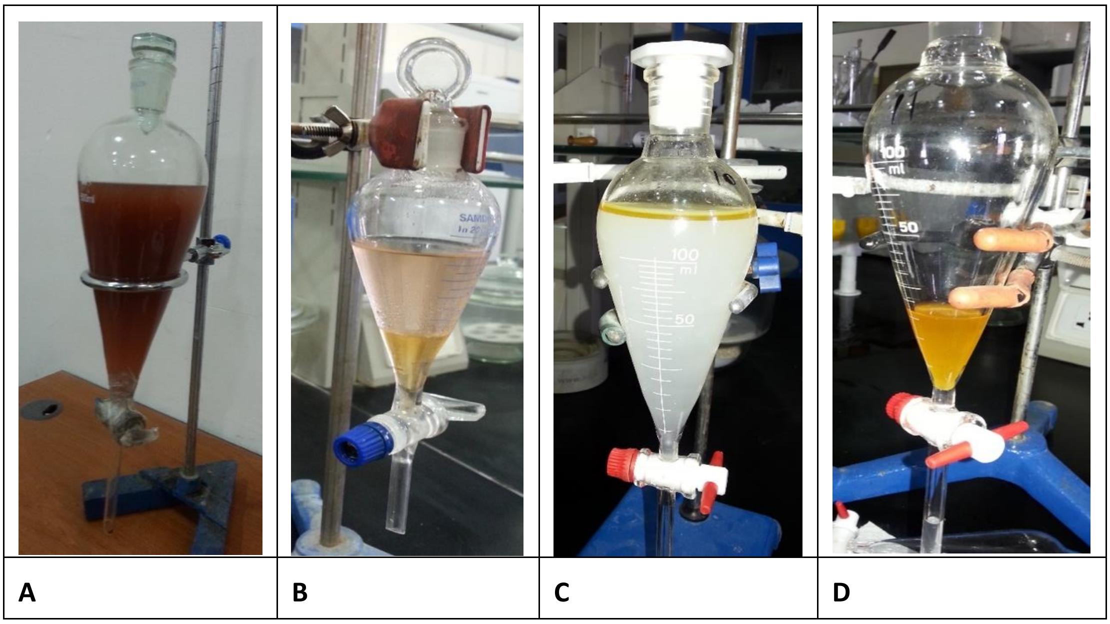


Figure 3-9. Steps of separetion the TE product mixture, A, all mixture befor separation. B, separeation of glycerol. C,washing the ester layer by warm water. D, pure Camelina ME

A rotary evaporator was used to remove excess methanol that might have been carried over during the washing process. Finally, the product of FAMEs was weighted and collected with some amounts of molecular sieves to make sure to get rid of the remnants of moisture content in a dark glass container and kept in the refrigerator.

3.6.2 Experimental Design Using RSM

RSM was separately used as optimization tool for transesterification TE for the oil extracted from raw Camelina seeds, and the oil extracted from DIC texturing Camelina seeds.

Three-parameter Central Composite Design CCD with 2^3 =8 factorial points, 3*2 star-points and 5 repetitions of central point, was used to optimize the TE transformation parameters (time of reaction, solvent/ oil and acid/solvent ratios) for the oils extracted from Camelina raw materials and Camelina DIC-treated seeds. 32 experiments were designed and conducted for the transesterification; 19 for transesterification of the raw seeds, and 13 experiments for the transesterification of the DIC treated seeds.

3.6.2.1 Experimental Design of TE for the Oil Extracted from Raw Un-Treated Camelina Seeds

19 experiments were conducted throughout a central composite design devoted to the raw Camelina seeds at different transesterification parameters. Table 3-3 shows the coded and natural levels of the independent variables employed; reaction time (h), ratio of Solvent / Seeds (ml/g) and ratio of Catalyst/ Solvent (v/v %).

Table 3-3. Real and coded values of independent parameters (solvent/seeds ratio, acid catalyst concentration, and reaction time) for TE of the raw Camelina *seeds*

Coded level	**-α**	**-1**	**0**	**+1**	**+α**
T: reaction time (h)	0.5	1.85	3.75	5.68	7
S: Solvent / oil ratio (ml/g)	3	6	10	14	17
C: Catalyst/ Solvent (v/v) %	1%	2.3%	5.5%	8.7%	10%

3.6.2.2 Experimental Design for the DIC-Textured Camelina Seeds

After defining and optimizing Transesterification (TE) conditions for raw un-treated Camelina seeds, which were: reaction time 36.6 min., solvent/oil volume ratio 17:1, and catalyst to solvent percent (2.0%) at constant temperature 60 °C and agitation 600 rpm. A 3-parameters, 5-level experimental design of 13 experiments was used to study the impact of DIC texturing on FAMEs yield. Table 3-4 shows the independent variables and their coded and natural levels employed in central composite design to optimize the effect of DIC processing temperature and treatment time on TE process.

Table 3-4. Independent variables and their coded and natural levels employed in central composite design to optimize the effect of DIC processing temperature and treatment time on TE process

Coded level	**-α**	**-1**	**0**	**+1**	**+α**
DIC processing temperature T (°C)	115.0	122.3	140	157.7	165.0
DIC saturated steam pressure (MPa)	0.17	0.21	0.36	0.58	0.7
DIC Treatment Time t (s)	15.0	19.4	30.0	40.6	45.0

3.6.3 *In-situ* Transesterification Process (ISTE)

In the current work, a comparative study has been conducted on Camelina seeds. The *in-situ* transesterification processes for producing Camelina biodiesel have been modeled and optimized using response surface methodology. The *in-situ* transesterification processes were conducted in a laboratory-scale setup; solvent type Methanol: Toluene (90:10), reaction temperature of 60˚C, agitation speed 600 rpm, and reaction time of 2 h, catalyst type H_2SO_4, were applied based on the process condition adopted in literature [282].

With the objective to identify conditions of the highest yield (Y) of Fatty Acid Methyl Esters FAMEs, the impact of the ratio of solvent to raw Camelina seeds solvent/seeds (S) and acid catalyst concentration (C), were studied as experimental parameters. Preliminary experiments allowed to identify the ranges of S from 10:1 to 50:1 (v/w) and C from 1% to 10% (v/v of solvent).

Each trial started by separately preparing a reactive mixture with adequate amounts of both solutions of methanol/toluene and acid catalyst in a 500-mL round bottom flask with reflux condenser. This mixture was then placed in the magnetic stirrer hot plate (LabT Ech, Korea), shaken at 600 rpm until the catalyst was completely dissolved, and at the same time, pre-heated to the desired reaction temperature (60 °C).

Simultaneously, an adequate quantity of Camelina seeds, was soaked in 10 ml of the reactive mixture and placed in a beaker for 10 minutes. When the methanolic/catalytic solution had reached the desired temperature, the mixture of Camelina seeds and methanol solution was introduced into the solution. The main step of the reaction was achieved by keeping temperature at 60˚C and mechanical mixing at constant speed 600 rpm for 2 hr. afterwards, the reaction was completed by allowing the round bottom flask to cool to room temperature. The cooled mixture was filtered, and sodium hydroxide was added to the liquid part to neutralize the acid catalyst, thus ensuring that the transesterification reaction had completely stopped.

A comparative study of ISTE was carried out, ISTE for fresh Camelina seeds has been optimized, and then the results of optimum ISTE reaction conditions were applied for DIC-textured Camelina seeds to optimize the DIC operation conditions. Based on literature data [248], and after some preliminary experiments, it had been decided to keep both of vacuum level and pressure drop rate constant at (3.5 kPa) and (65 MPa.s^{-1}) respectively. Consequently, the former operating variables were applied in a set of experiments designed using RSM to optimize and model the effect of DIC temperature T (°C) and processing time t (s), on biodiesel yield produced from DIC-Textured seeds.

The ranges of these independent variables T and t were also defined as 115-165 °C and 15-45 s, respectively. Moreover, it is worth highlighting that the treatment temperature is strictly correlated with the saturated steam pressure.

3.6.3.1 RSM for **In-situ** *Transesterification*

RSM was separately used as optimization procedure for *in-situ* Transesterification ISTE for fresh raw Camelina seeds, and DIC textured Camelina seeds.

2-parameter CCD (Central Composite Design) with 2^2=4 factorial points, 2*2 star-points and 5 repetitions of central point was used to optimize solvent/seeds ratio and acid catalyst ratio of ISTE reaction for the raw Camelina seeds, while another 3-factorial CCD was adopted to optimize the DIC operating parameters for ISTE of the DIC-textured seeds.

3.6.3.2 Experimental Design of ISTE for Fresh (Un-textured) Camelina Seeds

The coded and natural levels of the central composite design CCD devoted to the raw Camelina seeds for different *in-situ* transesterification experiments are listed in

Table 3-5.

Table 3-5. Real and coded values of independent parameters (solvent/seeds ratio S and catalytic acid concentration C) for in-situ *Transesterification for the raw* Camelina *seeds*

Coded level	**-α**	**-1**	**0**	**+1**	**+α**
S: Solvent / Seeds (ml/g)	10	15.9	30	44.1	50
C: Catalyst/ Solvent (v/v %)	1%	2.3%	5.5%	8.7%	10%

3.6.3.3 Experimental Design for ISTE for (DIC-textured) Camelina Seeds

After optimizing the *in-situ* transesterification (ISTE) conditions for the raw untreated Camelina seeds, another 2-parameter 5-level central composite design was adopted to study the effect of DIC operating parameters on FAMEs yield. 13 DIC-textured samples were *in-situ* transesterified using the optimized conditions (catalyst: solvent, 10% v/v) and (solvent/seed ratio, 50:1 v/wt.) estimated from the Response Surface Modeling (RSM) of the data listed in Table 4-15. The investigated DIC operating variables were treatment temperature, T and processing time, t. the coded and natural levels of the independent DIC parameters are listed in Table 3-6. In this same table, the levels of saturated steam pressure, which was not included as independent RSM parameter, are listed just to express the normal close dependence between the values of the temperature T and the pressure P of the saturated dry steam.

Table 3-6. Real and coded values of DIC independent parameters (processing temperature, T and processing time, t) to optimize the effect of DIC processing Parameters on ISTE treatment

Coded level	**-α**	**-1**	**0**	**+1**	**+α**
DIC processing temperature T (°C)	115.0	122.3	140	157.7	165.0
DIC saturated steam pressure (MPa)	0.17	0.21	0.36	0.58	0.7
DIC Treatment Time t (s)	15.0	19.4	30.0	40.6	45.0

3.7 Assessment Methods of FAMEs

3.7.1 FAMEs Profiles by Gas Chromatography

Analyses of FAMEs were performed using a GC 2010 (Shimadzu, Japan). This gas chromatograph is equipped with flame ionization detector, and a Capillary Column SP 2380 (30 m, 0.25 mm, 0.20 µm) poly (90% biscyanopropyl/10% cyanopropylphenyl siloxane). Nitrogen was used as the carrier gas at Injector Volume 1 µL, Injector Temperature 250 °C, Detector temperature 270 °C. Oven temperature 150 – 230 °C (4C/min). FAMEs were identified and quantified by comparing the retention times with those of FAME standards.

Standards were available for methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate purchased from Sigma-Aldrich, Supelco-CRM1891, F.A.M.E. Mix GLC-10, USA.

The ester content in the sample expressed as a mass fraction percentage, was calculated using Eq. 3-22 [238] and [283]:

$$\mathrm{m\%} = \frac{\mathrm{A}}{(\Sigma\,\mathrm{A_T})\ -\mathrm{A_S}} \qquad \textit{Eq. 3-22}$$

Where:

m% is the mass fraction in percent of the samples for each methyl ester (mg)

$\Sigma\,A_T$ is the total peak area from the samples methyl esters

A is the area under peak of specific samples MEs.

A_S is the area under peak of the same MEs in the external standards

3.7.2 Determination of the Biodiesel Physicochemical Properties of Fatty Acid Methyl Esters (FAMEs)

3.7.2.1 Measuring and estimation of Yield

The biodiesel yield (%) was calculated using Eq. 3-24:

$$\mathrm{Y(biodiesel\ yield)\%} = \frac{\mathrm{Weight\ of\ biodiesel\ (g)}}{\mathrm{Weight\ of\ seeds\ (g)}} \times \mathrm{Lipid\ content} \qquad \textit{Eq. 3-23}$$

3.7.2.2 Determination of FAMEs Density by Pycnometer (EN ISO 12185)

There are two methods to determine the density, using pycnometer and hydrometer. In our research, pycnometer was used as one of the most precise and accurate methods. Indeed, measuring the density by hydrometer is affected by many factors including temperature, alcohol present in biodiesel, etc. making measurements not accurate.

To calculate density of biodiesel, mass of empty pycnometer, mass of pycnometer with biodiesel sample are recorded. Density of biodiesel sample is calculated using the formula in below [284].

$$\text{Density of FAME} = \frac{\text{Weight of FAME}}{\text{Volume of FAME in pycnometer}} \qquad \textit{Eq. 3-24}$$

3.7.2.3 Determination of Specific Gravity and API Gravity of FAMEs

Specific gravity or Relative density (RD) is the ratio of the density of the material at a selected temperature to the density of a water at the same temperature, usually be 15.6 °C [285].

API gravity is defined by the American Petroleum Institute to characterize heavy and light weight fuel fractions. Although density, specific gravity, and API gravity are not included in specifications outlined in the ASTM standards for petrodiesel (D 975), biodiesel (D 6751) or biodiesel/petrodiesel blends (D 7467) a minimum API gravity at 30° is recommended to maintain good power production and fuel economy for engine manufacturers [286]:

$$\text{Specific gravity, S. G.} = \frac{\text{Weight of Sample}}{\text{Weight of Equal Volume of Water}} \qquad \textit{Eq. 3-25}$$

$$\text{API} = \frac{141.5}{\text{SG at } (15.6^{\circ}\text{C})} - 131.5 \qquad \textit{Eq. 3-26}$$

3.7.2.4 Determination of FAMEs Kinematic Viscosity (ASTM D-445)

There are various instruments utilized within industry practice to accurately estimate and predict viscosity. These instruments include capillary viscometers which is most used to measure the viscosity of a transparent Newtonian liquid. It only requires a small volume portion of the liquid fuel. In this study, capillary viscometer (Viscometer, *Cannon Fenske Routine*, Eurostar Scientific LTD, PSL ASTM-IP 100, UK) was used, Kinematic viscosity determined by measured the time for a fixed volume of the liquid to flow through the capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The kinematic viscosity is then calculated from the measured flow time and the calibration constant of the viscometer [287].

3.7.2.5 Determination of FAMEs Acid Value (EN 14104)

The acid number of biodiesel samples was measured using titration methodology. The method in detailed was; 50 ml of Ethanol/Diethyl Ether solvent was added to 250 mL

Erlenmeyer flask, then 5 drops of phenolphthalein was added. Some drops of KOH solution were added using Micro-burette in order to neutralize the solvent until the color changed into light pink. Then some quantity of biodiesel was weighted (10g) and added to neutralize solvent then the titration was repeated until the mixture reach the desired color. The acidity of Camelina biodiesel were calculated with formula in Eq. 3-10, (Determination of oil Acid Value) [284].

3.7.2.6 Determination of FAMEs Iodine Value (EN 14111)

The iodine number is a measure for the number of double bonds in a sample. It specifies the quantities of iodine in gram that are consumed by 100 g of the biodiesel sample under the specific conditions. The determination of the iodine value by titration with a solution of sodium thiosulfate is qualified by the European standard EN 14111. The iodine value is expressed in g of I/100g of biodiesel. The method in detailed was; 250 mL Erlenmeyer flasks and accurately weight 0.13-0.15 g of biodiesel samples was prepared, then a solvent was prepared by mixing equal volumes 200 mL of cyclohexane and acetic acid. Biodiesel was dissolved in 20 ml of prepared solvent and 25mL of *Wijs* reagent 0.1 mol/l was added using precision pipette and stopper, then the flasks was placed in the dark place and leaved for 1h. Then blank solution was prepared by mixing, 20 ml of solvent with 25 ml of *Wijs* reagent and without adding biodiesel sample. At the end of 1 h, 20 ml of potassium iodide solution and 150 ml of ultra-pure water were added then titrated with standard sodium thiosulfate solution ($Na_2S_2O_3$) with concentration 0.101 mol/l. titration was contained until reaching the yellow color, then 8 drops of starch solution was added and titrated until the mixture was reached the light grey color. Iodine value of biodiesel calculated with formula in Eq. 3-21.

3.7.2.7 Determination of FAMEs Cetane Number (ASTM E1655)

The chemical and physical properties of fuel play important role in delay period of fuel combustion. The cetane number (CN) of the fuel is the most significant parameter which is responsible for the delay period [288]. The higher the carbon chain length, the higher the cetane number. Thus cetane number usually accepted by diesel engines should be ranged between (40) and (55) [289]. In this study, Cetane number was determined by (*Zeltex 101C*, Portable Near-Infrared Octane/Cetane Analyzer, Hagerstown, MD 21740, USA). The method was; Turn on the *ZX-101C*, then “Zero Adjust” was pressed, then the sample was placed in the *ZX-101C* jar and Octane Number was displayed and printed [290].

This method uses a Near Infrared (NIR) analyzer to obtain the absorption spectrum of diesel which then is fed to a chemometric model to estimate cetane number [291].

3.7.2.8 Determination of FAMEs Conradson Carbon Residue (D 189)

Numerous Equivalent Test Methods (IP 13, ISO 6615, DIN 51551, JIS K 2270, and AFNOR T60-116) can be used to assess the value of carbon residue issued from burning fuel using Conradson Carbon Residue Figure 3-10. This is an approximation of the fuel tendency to compose deposits in vaporizing pot-type and sleeve-type burners.

The method in detailed was; a weighed quantity of sample was placed in a crucible and subjected to destructive distillation. Then the residue undergoes cracking and coking reactions during a fixed period of severe heating. At the end of the specified heating period, the carbonaceous residue was produced in the test crucible, then this carbonaceous residue was cooled in a desiccator and weighed. The residue remaining was calculated as a percentage of the original sample, and reported as Conradson carbon residue [292].

Figure 3-10. Conradson Carbon Residue

3.7.2.9 Determination of FAMEs Cold Filter Plugging Point (CFPP) (ASTM D 6371)

The Cold Filter Plugging Point (CFPP) of a fuel is suitable for estimating the lowest temperature at which a fuel will give trouble-free flow in specific fuel systems. CFPP determinations were performed according to ASTM D 6371, using a cooler bath (bath coupled with rotary evaporator (*BUCHI R-215*, Swiss). The test is conducted such as a specimen of the sample were poured into a test jar up to the line indicating sample height (approximately 45 ml). For CFPP determinations, samples were cooled to approximately -12.7 °C above the anticipated plugging point and drawn into a pipette under controlled vacuum through a standardized wire mesh filter. Sample cooling was continued and the test procedure repeated until the sample could no longer fill the pipette in 60 seconds. This test method is technically equivalent to test methods IP 309 and EN 116 [293], [292] and [294].

3.7.2.10 Determination of FAMEs Pour Point (ASTM D 97)

Pour point determinations were performed according to ASTM D 97 using a manual refrigerated bath (bath coupled with rotary evaporator (*BUCHI R-215*, Swiss). Briefly, Camelina biodiesel were poured into a test jar up to the line indicating sample height (approximately 45 mL). Beginning at 9.0°C above the expected pour point, the samples were tested for pour point by briefly removing the sample from the bath, tilting to the side, and observing any movement of sample. The test was repeated until no movement of sample was observed upon holding the sample horizontally for 5 seconds [293] and [292].

3.7.2.11 Determination of FAMEs Cloud Point (ASTM D 2500-02)

Cloud point is the temperature of a liquid sample when the smallest observable cluster of wax crystals first appears upon cooling under fixed conditions. The apparatus for determination of cloud point consists of a cylindrical glass test jar, thermometers, and cooling bath. The temperature of the test sample is first elevated at least 14°C above the anticipated cloud point. Presence of moisture content in the apparatus is removed using dry lint-less filter paper. The cooling bath temperature is maintained at 0 ± 1.5°C. Each test is taken at the multiples of 1°C, until the fuel candidate shows a cloud of wax crystals in the test jar. The standard also states that a wax cloud always forms first at the bottom of a test jar where the temperature of the fluid is lowest [295].

3.7.2.12 Determination of FAMEs Freezing Point

Freezing point increases with molecular weight, and is strongly influenced by molecular shape. Molecules that fit more readily into a crystal structure have higher freezing points [285].

Freezing point determined by (Oil Product Low-temperature Characteristics Meter – *OPLCM, SHATOX Co. LLC* Russian Federation, Tomsk) meet all ISO 9001 requirements Figure 3-11.

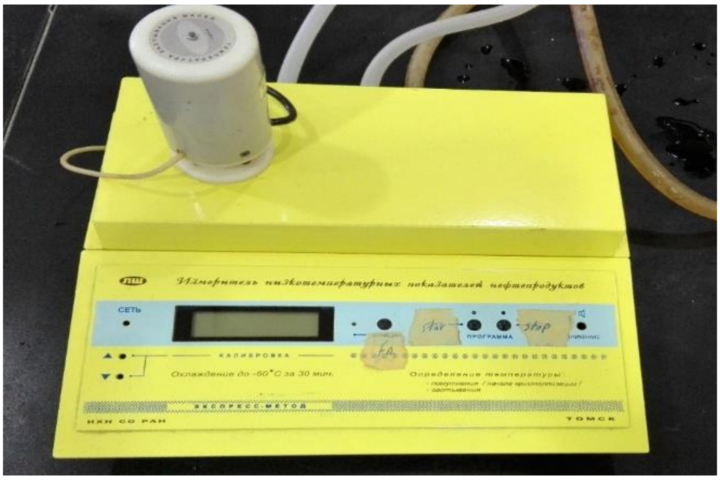


Figure 3-11. Oil Product Low-temperature Characteristics Meter – OPLCM, SHATOX Co.

The test method was conducted as the following: after insertion of 25 ml of the sample into a test chamber, the sample is cooled while being continuously stirred and monitored by an optical system. The temperature of the specimen is measured with an electronic temperature measuring device. When crystal formation is detected in the specimen, the temperature is recorded and the specimen in the test chamber is allowed to warm, while being continuously stirred and monitored, until the crystals in the specimen completely disappear. The temperature of the specimen when the last crystals disappear is recorded as the freezing point (automated method) [296].

3.7.2.13 Determination of FAMEs Flash Point (ASTM D 93)

Flash point is the tendency of the test specimen to form a flammable mixture with air under controlled conditions. Flash point test methods include IP 34, ISO 2719, DIN 51758, JIS K 2265, and AFNOR M07-019. The Flash point was determined by (GD-261-

1 Pensky-Martens Closed Cup Flash Point Tester Chongqing Gold Mechanical & Electrical Equipment Co., Ltd, China), Figure 3-12.

Figure 3-12. Pensky-Martens Closed Cup Flash Point Tester

The test carried out by heating the sample at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which the vapor above the sample ignites [292].

3.7.3 ASTM Distillation (ASTM D 1160) [297]

The biodiesel specification for the vacuum distillation Figure 3-13, procedure is described in ASTM D 1160. The biodiesel specification, ASTM D 6751, specifies 360°C as the maximum T-90 temperature; the temperature at which 90% of a 200 ml sample has been distilled. This test was developed to determine the distillation characteristics of petroleum products and was chosen by ASTM to be included in the biodiesel specification.

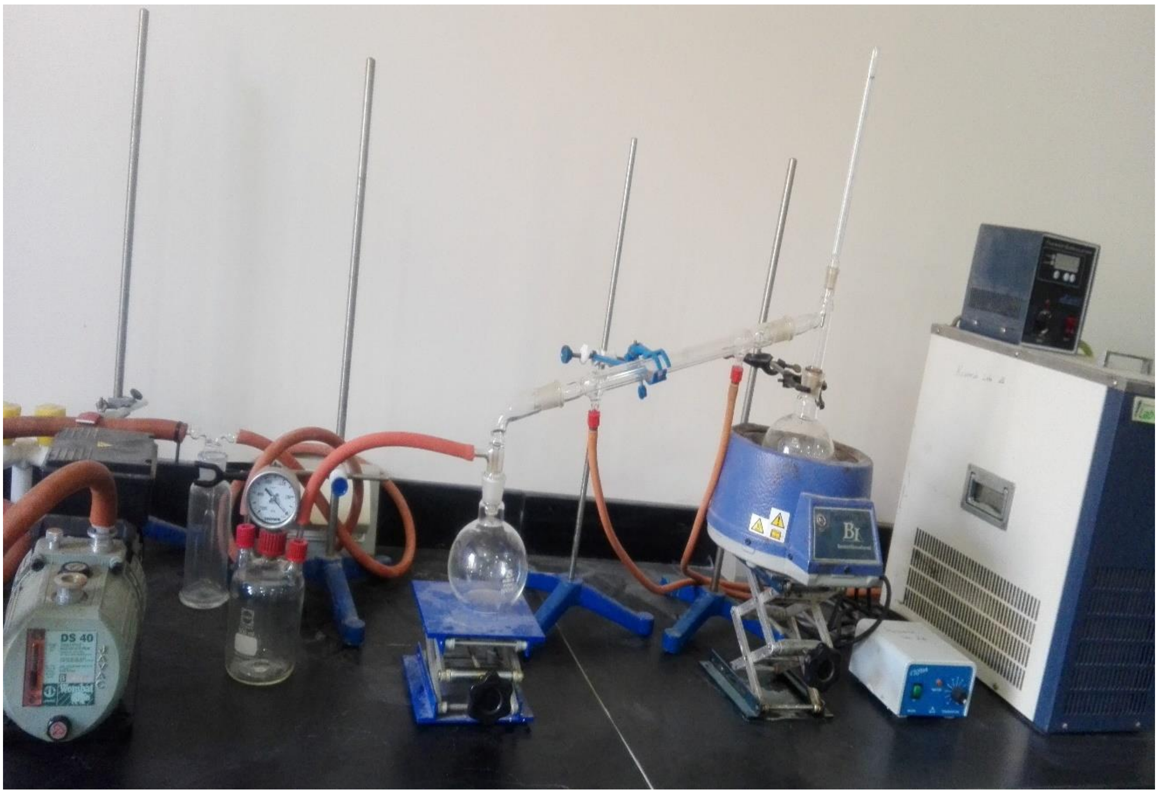


Figure 3-13. Vacuum Distillation Apparatus

A sample of FAMEs which has been produced from DIC-TE process is distilled under vacuum and the temperature at which each 10% increment has been distilled is noted until all the sample is boiled off and condensed. The data were compared with those of distillation for petroleum-derived diesel fuel. The petroleum diesel used in this work was obtained from the laboratory of Kirkuk petroleum fields. The boiling range of the fuels is directly related to viscosity, vapor pressure, heating value, average molecular weight, as well as other chemical, physical, and mechanical properties [298].

CHAPTER 4. RESULTS AND DISCUSSION

The results obtained throughout the current work are categorize as the following:

4.1 Moisture Content for Camelina Seeds

The importance of determination the moisture content come from its direct relation with the seeds storage conditions. Camelina seeds moisture content should be less than 8% wb for best storage [66].

Moisture content, in general, has a direct effect on oil yield; it has been reported that increasing the seeds moisture content leads to decrease the oil recovery [299].

However, the maximum oil contents in the seeds is related to seeds moisture content for example, the maximum oil contents in Soybean, Sunflower and Rapeseed is related to moisture content 13%, 12%, and 10.5% wb, respectively [300], [262] and [301].

Moisture in biomass generally stored in spaces within the dead cells and within the cell walls. For seeds safe storage, it is necessary to reduce the moisture content of the seeds. In order to warranty suitable storage, the seeds should have appropriate moisture content. Thus, the seeds should be dried to the correct moisture content, the dry steps are necessary due to that the moisture content also has a noticeable effect on the heating value. Moreover the extension in time of high moisture content in the seeds will affect the oil quality due to promoting the hydrolysis of triglycerides, that's lead to generating free fatty acids and reducing the shell life of the oil [1] and [302].

In the current research, the moisture content was measured for DIC-textured and un-textured Camelina seeds by IR moisture content analyzer and oven at 105°C for 24 h, the values are recorded in Table 4-1.

Table 4-1. Percentage of moisture content dry basis by W (g H_2O/g db) by oven and IR analyzer

Sample No.	W (Oven)	W (IR analyzer)
Completely dried material	0.00	0.00
Control	0.0465	0.0420
DIC 1	0.0461	0.0340
DIC 2	0.0497	0.0453

DIC3	0.0488	0.0406
DIC4	0.0529	0.0387
DIC5	0.0502	0.037
DIC6	0.0488	0.0445
DIC7	0.0513	0.0339
DIC8	0.0488	0.0431
DIC9	0.0497	0.0430
DIC10	0.0495	0.0391
DIC11	0.0539	0.0515
DIC12	0.0492	0.0414
DIC 13	0.0508	0.0435

Based on the results recorded in the Table 4-1, the correlations between the two different measurements of moisture content dry basis by oven and the IR analyzer methods are illustrated in Figure 4-1. It shows that the measurements performed through oven systematically had greater value than the IR moisture analyzer. This may be due to that the IR analyzer has less capacity to measure the moisture content of the entire product such as it is capable to directly access only to the surface moisture. This phenomenon is a one of the major drawbacks of the IR moisture analyzer, also there is little air movement through the cup, and hence almost no moisture content is lost. So IR analyzer always needs to be initially well calibrated for each material [303] and [304]; it also be used for great variation ranges of water content to not concern great relative variations.

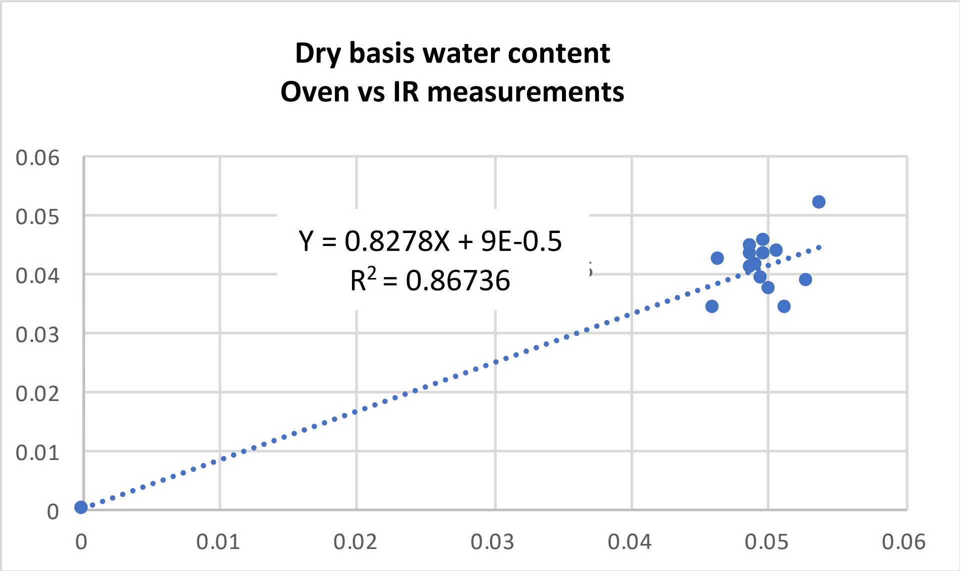


Figure 4-1. Relation between %dry basis moisture content determined by oven vs IR analyzer

Moisture content has an effect on some oil quality parameters, such as saponification value, iodine value, free fatty acid, acid value and color [305]. The moisture content of the investigated samples ranged from (0.0461 to 0.0539 g H_2O/g db) as minimum and maximum value.

4.2 Oil Yield

Usually in oil extraction process; cold-pressing is preferred more than solvent extraction due to keeping more health beneficial components such as antioxidants [306], [307] and [308]. The factors affect the increase of pressure and temperature in the screw barrel have great positive influence on oil yield. Those factors include the diameter of the restriction die (nozzle) located at the meal discharge and by screw rotation speed (the higher the speed and the bigger the restriction opening, the lower the yield) [309], [310] and [311].

Thus, choice of suitable nozzle die meters and suitable type of pressing instrument are very important to obtain highest oil yield.

In solvent extraction, during the contact time between seeds and solvent, two main stages take place. The first one is washing stage, this stage concerns the oil positioned on the product surface, which is normally easily and quickly removed at the beginning of the extraction process, thus this stage described as fast process. The second stage is diffusion, which is described as the slow process. this stage passage through two mechanisms: slow, unhindered diffusion of oil held in the ruptured cells in the seed; and very slow, hindered diffusion of oil held within un-ruptured cells in the seed [312].

DIC allows the seeds structure to be more expanded with more effective washing stage and higher diffusivity, thus, allowing solvent extraction to be undertaken very efficiently in a shorter time using lower quantity of solvent [313], [143] and [314].

The values of oil yield extracted from the seeds (by mechanical pressing and solvent extraction) are presented in Table 4-2 and Table 4-3 respectively.

Camelina s. seeds treated by DIC at (Steam Temperature T: 157.7°C and treatment time: 40.6 s) give the highest oil yield extracted by the two methods compared to raw material. The maximum oil yield accounts (for sample DIC5) were about 0.3153 and 0.4490 g oil/g dry seeds from pressing and solvent extraction processes, respectively.

This means an increasing of oil extraction by about 38% and 22% compared to the untreated seeds, for seed pressing and solvent extraction processes, respectively.

Table 4-2. Oil yield from mechanical pressing yield

Sample	Oil by pressing		
	g oil/ g wet seeds	g oil/g db DB	% of yield (DIC-seeds Yield/un-treated seeds Yield)
Control	0.218	0.2277	100%
DIC 1	0.281	0.2936	129%
DIC 2	0.230	0.2421	106%
DIC3	0.280	0.2952	130%
DIC4	0.278	0.2927	129%
DIC5	0.300	0.3153	138%
DIC6	0.233	0.2449	108%
DIC7	0.278	0.2930	129%
DIC8	0.273	0.2859	126%
DIC9	0.255	0.2679	118%
DIC10	0.267	0.2818	124%
DIC11	0.276	0.2911	128%
DIC12	0.265	0.2787	122%
DIC13	0.250	0.2635	116%

Table 4-3. Oil yield from solvent extraction for Camelina *seeds*

Sample	Oil by solvent extraction		
	g oil/ g wet seeds	g oil/g db DB	% of yield (DIC-seeds Yield/un-treated seeds Yield)
Control	0.353	0.3681	100%
DIC 1	0.411	0.4296	117%
DIC 2	0.418	0.4379	119%
DIC3	0.421	0.4430	120%
DIC4	0.407	0.4277	116%
DIC5	0.428	0.4490	122%
DIC6	0.398	0.4169	113%
DIC7	0.404	0.4253	116%
DIC8	0.374	0.3918	106%
DIC9	0.407	0.4267	116%
DIC10	0.400	0.4205	114%
DIC11	0.400	0.4208	114%
DIC12	0.381	0.4001	109%
DIC13	0.397	0.4168	113%

4.3 Moisture and Oil Content of Camelina Cakes

Seed pressing leaves a considerable amount of residual oil in the oil cake/ meal, therefore, the resulted pressed cake was subjected to solvent extraction process to recover the residual oil [51].

The advantage of pre-pressing is that a press cake is formed from the seeds which allow a good solvent contact and percolation in the extractor. Extraction by combining screw press and solvent extraction has the economic advantages of low costs and higher oil yield than single solvent extraction [315].

The purpose of pressing of the seeds cake is to squeeze out as much liquid as possible from the solid part. This is important not only to improve the oil yield and the quality of the meal but also to reduce the moisture content of the press cake as much as possible, thereby reducing the fuel consumption of the driers and increasing their capacity [316].

Table 4-4. Impact of DIC on moisture content of Camelina cake (measured by oven method)

Sample No.	Processing temperature °C	Processing time (s)	Moisture content (g H_2O/g db)	Impact of DIC treatment on moisture content (g H_2O/g db)
Control	/	/	0.0152	0
DIC 1	140.0	30.0	0.0148	-0.0004
DIC2	165.0	30.0	0.0134	-0.0018
DIC 3	140.0	45.0	0.0078	-0.0074
DIC 4	140.0	30.0	0.0039	-0.0113
DIC 5	157.7	40.6	0.0052	-0.01
DIC 6	157.7	19.4	0.018	0.0028
DIC 7	140.0	30.0	0.0334	0.0182
DIC 8	122.3	19.4	0.0064	-0.0088
DIC 9	122.3	40.6	0.0078	-0.0074
DIC 10	140.0	30.0	0.0138	-0.0014
DIC 11	115.0	30.0	0.0054	-0.0098
DIC 12	140.0	15.0	0.0087	-0.0065
DIC 13	140.0	30.0	0.0166	0.0014

It is worth mentioning that the press oil yield depends on the moisture content [317]. Table 4-4 shows the moisture content measured by oven for Camelina cake issued from seed pressing. Moreover, the values of moisture contents versus DIC treatment reveal there was almost the same quantity. The relations between the moisture content (dry basis) for cakes and seeds are shown in Figure 4-2.

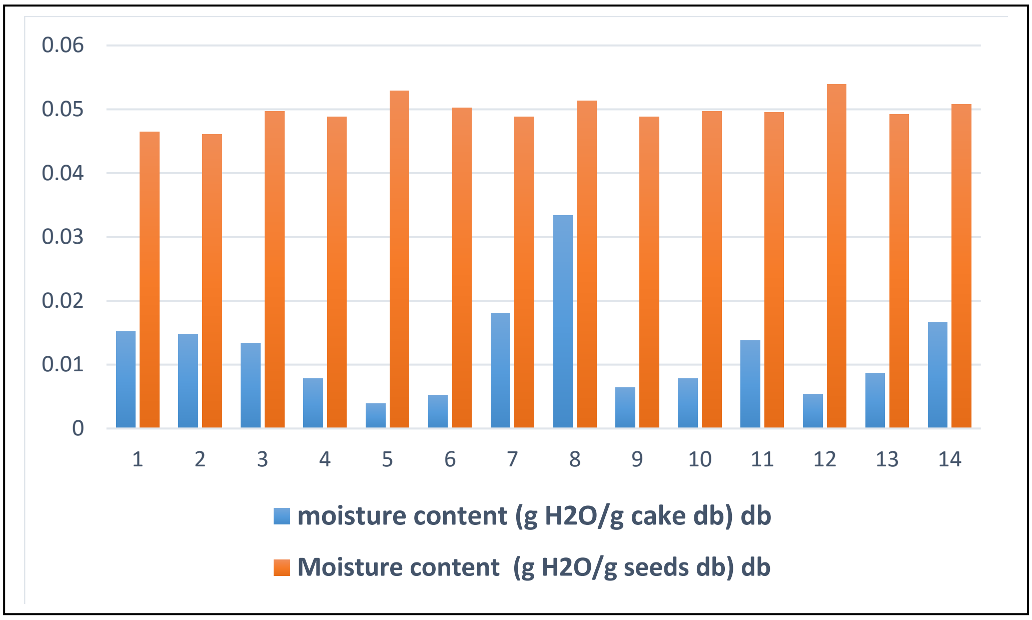


Figure 4-2. Relation between dry basis moisture content for seeds and cake (g H_2O/g db)

From the data in Table 4-5 and Table 4-4, the dry basis moisture content of the cakes and the seeds were 19.7% and 20.0 respectively.

Figure 4-2 shows remarkably the differences in moisture content between the DIC treated cakes and seeds. The lower value of the moisture content in the cakes may be attributed to releasing of most of the moisture content from the cakes during the pressing process. Table 4-5 shows the part of oil extracted from cake by solvent extraction.

Table 4-5. Yield of cake oil obtained by solvent-extraction

Sample No.	Oil g/g db cake
Control	0.0929
DIC1	0.0687
DIC2	0.0845
DIC3	0.0650
DIC4	0.0709
DIC5	0.0585
DIC6	0.0784
DIC7	0.0697
DIC8	0.0778
DIC9	0.0629
DIC10	0.0715
DIC11	0.0733
DIC12	0.0702
DIC13	0.0687

Table 4-5 shows that the highest oil yield was from Camelina raw materials cake (0.0929 g oil/g db cake) compared to all other DIC treated Camelina cakes, while the lowest oil yield (0.0585 g oil/g db cake) was for the cake produced from DIC treated seeds (Experiment number DIC5). The findings confirmed that obviously, a high yield of oil gives cake with a lower residual oil content [123].

4.4 Effect of DIC Parameters on Oil Extraction of Camelina Seeds and Cakes

The oil yield was calculated for all the experiments carried out under different DIC condition following the experimental design adopted in the recent work. The yield of the oil extracted by pressing and solvent extraction from the DIC treated seeds and by solvent extraction from the DIC treated cakes is recorded in Table 4-6. Since a limited quantity of seeds was used (200 g) in the process of pressing, the amount of residual seed oil lost in the screw cage has a significant effect on the percentage of the values of oil pressing yield as shown in Table 4-6. Therefore, the use of some tons of seeds in the process (as in the industrial scale) will reduce the effect of such a loss on the real yields of final product oil.

The effect of DIC operating variables on oils yield are expressed in Pareto chart, Main Standardized effect and response surface charts estimated by Response Surface Modeling, RSM shown in Figure 4-3.

Table 4-6. Experimental design with the actual values of the DIC independent variables, and oil yield extracted by pressing and solvent.

Run	Tem. °C	time (s)	Oil solvent extracted from seeds (g oil/g db)	Oil from seeds pressing (g oil/g db)	Oil from cake solvent extracted (g oil/g db)
Control	/	/	0.3681	0.2277	0.0929
DIC1	140	30	0.4296	0.2936	0.0687
DIC2	165	30	0.4379	0.2421	0.0845
DIC3	140	45	0.4430	0.2952	0.0650
DIC4	140	30	0.4277	0.2927	0.0709
DIC5	157.7	40.6	0.4490	0.3153	0.0585
DIC6	157.7	19.4	0.4169	0.2449	0.0784
DIC7	140	30	0.4253	0.2930	0.0697
DIC8	122.3	19.4	0.3918	0.2859	0.0778
DIC9	122.3	40.6	0.4267	0.2679	0.0629
DIC10	140	30	0.4205	0.2818	0.0715

DIC11	115	30	0.4208	0.2911	0.0733
DIC12	140	15	0.4001	0.2787	0.0702
DIC13	140	30	0.4168	0.2635	0.0687

Table 4-7. Empirical models and regression coefficients for oil yields Y_A, Y_B, and Y_C expressed in (g oil/g db), versus DIC operating parameters: Temperature (T) and treatment time (t). (A) Oil extracted by pressing from DIC treated seeds, (B) oil extracted by solvent from the pressed cake, and (C) oil extracted by solvent from DIC treated seeds.

$\mathrm{Y_A} = 0.2796 + 0.00384\mathrm{T} - 0.0164\mathrm{t} - 0.00003\mathrm{T}^2 + 0.0002\mathrm{Tt} + 0.00001\mathrm{t}^2$	*Eq. 4-1*
$\mathrm{Y}_B = 0.2495 - 0.00288\mathrm{T} + 0.00156\mathrm{t} + 0.00003\mathrm{T}^2 - 0.000007\mathrm{Tt} - 0.00002\mathrm{t}^2$	*Eq. 4-2*
$\mathrm{Y_C} = 0.3738 - 0.0008\mathrm{T} + 0.0033\mathrm{t} + 0.000005\mathrm{T}^2 - 0.000004\mathrm{Tt} - 0.00002\mathrm{t}^2$	*Eq. 4-3*

Table 4-8 shows the mathematical models estimated from RSM of oil yields Y_A, Y_B, and Y_C expressed in (g oil/g db), versus DIC operating parameters: Temperature (T) in °C and treatment time (t) in s, Also the R^2 value to be 71.4%, 68.0%, and 92.5%, respectively. They concern oil extracted by pressing from DIC treated seeds, oil extracted by solvent from the pressed cake, and oil extracted by solvent from DIC treated seeds, respectively.

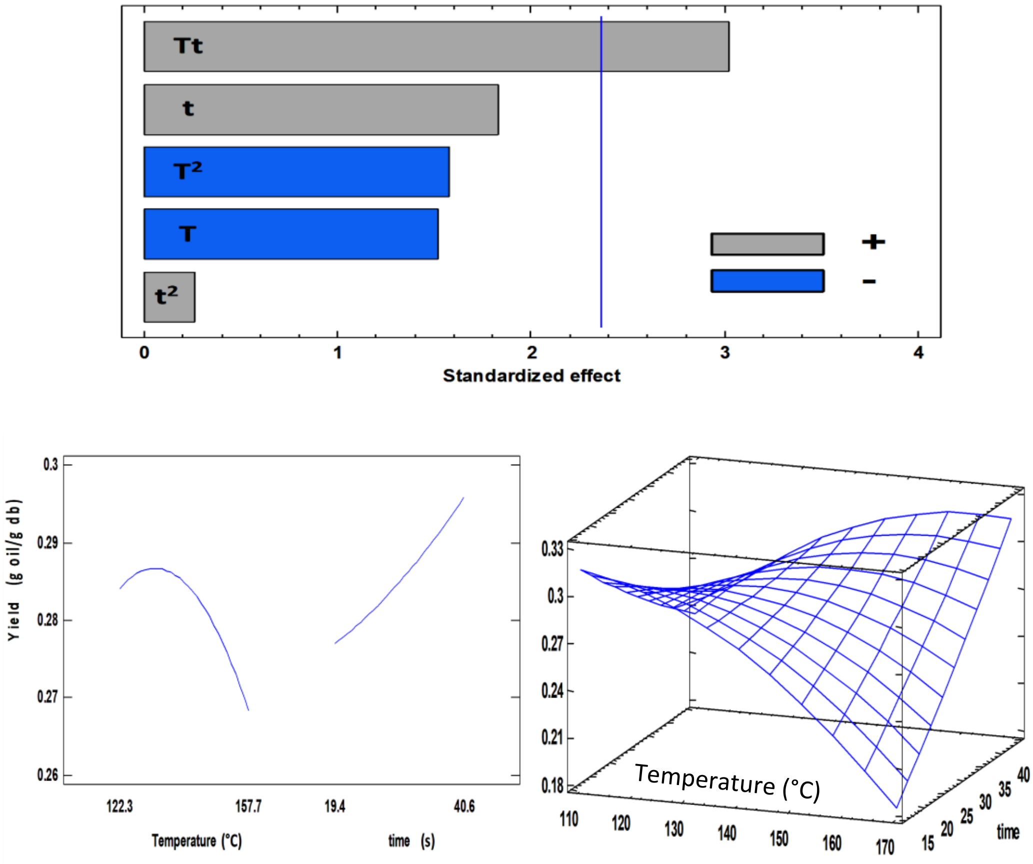


Figure 4-3. Pareto chart, main effect plots, and response surface for yield of oil extracted by pressing from DIC treated seeds

Pareto chart Figure 4-3 illustrates the significance of DIC parameters on yield of the oil extracted from DIC-textured seeds by pressing. It shows that the most effective term was the effect of the interaction between T and t, while individually, the linear and quadratic terms of each parameter were not significant. The general trend and response surface plot showed that as DIC temperature increases, the oil yield decreases, while as treatment time increases, oil yield increases. The estimated regression coefficient (R^2 = 71.4%) confirmed that the adopted model is moderately capable to explain the experimental results. It is worth noting that an optimum experimental value of yield of oil (YA) = 0.3153 g oil/ g seeds db was achieved at: (T = 157.7 °C and t = 40.6 s). This value is 38.5% greater than that for the untreated raw material, which gave a yield of 0.2277 g oil/g seeds db. The RSM results showed that an optimum oil yield value (0.316 g oil/ g seeds db) was achieved at (T = 163.7 °C and t = 45.0 s).

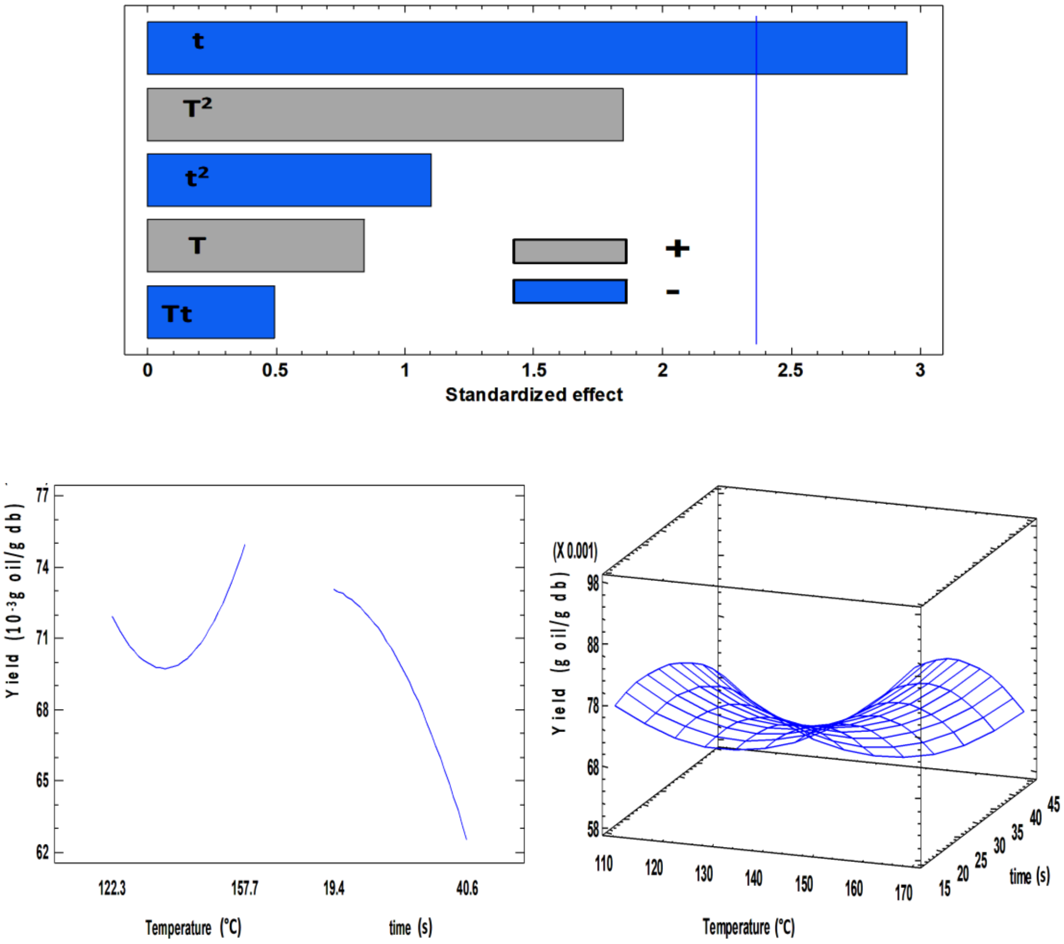


Figure 4-4. Pareto chart, main effect plots, and response surface for yield of oil extracted by solvent from pressed cake

Figure 4-4 reveals the RSM for the yield of the oil extracted by solvent from the cake resulted from pressing of the DIC-textured seeds. Pareto chart with ANOVA of 0.05 showed that processing temperature has non-significant effect while processing time has significant and negative effect on oil yield. This means that the lower the treatment time, the higher the remaining oil in the cake. The greatest oil yield was obtained with the cake which produced from pressing Camelina un-textured seeds (0.0929 g oil/g db), while (0.0585 g oil/g db) was extracted from cake produced from pressing Camelina DIC-textured seeds collected at T=157.7 °C and t=40.6 s; (exp. No. DIC5).

From the experimental data, an inverse relationship between oil yield from pressing the seeds and the residual oil yield in the cake has been developed with good coefficient of determination R^2 = 68.0%, which indicated good confidence for the relationship as shown in Figure 4-5.

$$Y = -0.2853X + 0.1513 \qquad \textit{Eq. 4-4}$$

Where Y is oil yield (g oil/g db) extracted from cake by solvent, and X is oil yield (g oil/g db) extracted from seeds by pressing.

From this correlation, the residual oil in the cake can be predicted for a particular oil yield extracted by pressing the seeds.

The above cited results indicated that DIC treatment induced highest pressing and diminished the residual oil in the pressed meal.

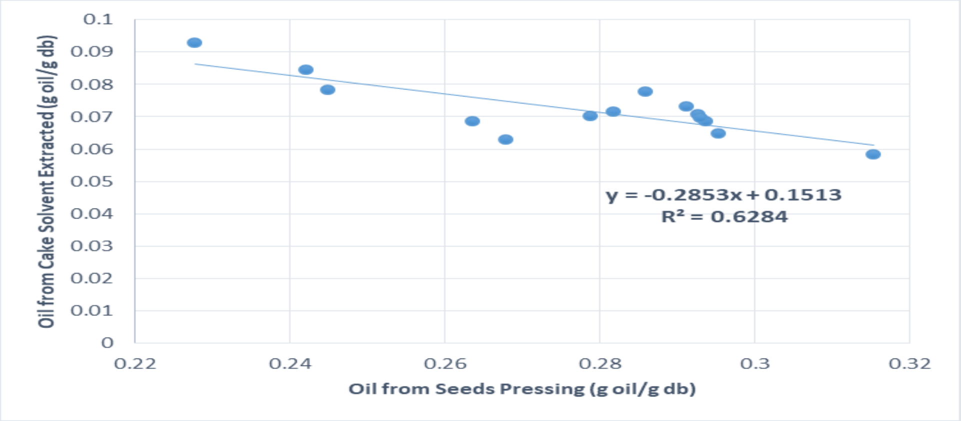


Figure 4-5. Evolutions of pressing yield and residual oil in the cake

Figure 4-6 shows Pareto chart for the significance of DIC parameters on yield of the oil extracted from DIC-textured seeds by solvent extraction. It reveals that both DIC processing time and temperature were significant with positive impacts on the oil yield, which means that the higher the DIC treatment time and temperature, the higher the yield of oil. However, in the studied ranges, the effect of DIC treatment time was more significant.

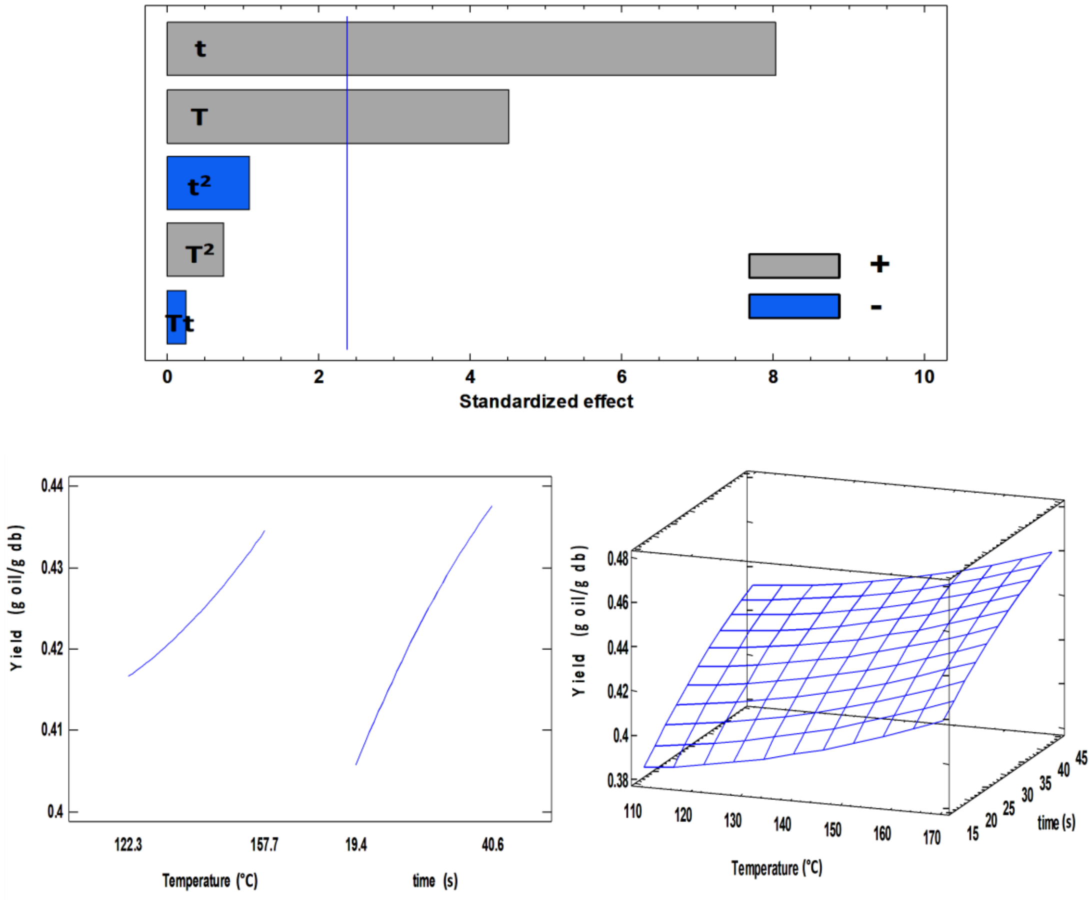


Figure 4-6. Pareto chart, main effect plots, and response surface for yield of oil extracted by solvent from DIC treated seeds where T: DIC Temperature, t: DIC treatment time

The relevant empirical mathematical model for oil extracted by pressing from DIC treated seeds and oil extracted by solvent from the pressed cake and DIC treated seeds, shown in Table 4-7 reflected a good regression coefficient (R^2 = 71.4 %) for pressing treatment seeds which confirms that the model has a good capability to explain the experimental results.

An optimum oil yield value (0.316886 g oil/g db) was obtained at DIC operating conditions: (T=163.7 °C and t = 45 s).

Also in

Table 4-7, it is worth mentioning the high regression coefficient (R^2 = 92.5%) for solvent extraction of treatment of seeds checking the high capability of the model to explain the experimental results. An optimum oil yield value (0.4563 g oil/g db) was obtained at DIC operating conditions: (T=165 °C and t = 45 s).

In contrast to results of the seeds oil extraction process (pressing and solvent extraction) and its high regression coefficient value, solvent-extracted oil from the pressed cake reflected low regression coefficient (R^2 = 68.0 %) meaning weak capability of the model to explain the experimental results. The difference in "initial" oil content in the cake samples should explain this observation. Indeed, the greater the amount of oil extracted from the seeds, the feebler the amount of oil remaining in the cakes. However, an optimum cake oil yield of 0.0848 g oil/g db was obtained at DIC operating conditions: T=165 °C and t = 15 s.

4.5 Physical and Chemical Characteristics of Oil

Physical and chemical characteristics of the oil produced from the un-textured and DIC-textured Camelina seeds by pressing were determined and presented in Table 4-9.

Table 4-9. Chemical and physical properties of oil from raw and DIC-treated Camelina *seeds, in comparison with other researches*

Properties	Oil from un-texture Seeds	Oil from DIC-textured seeds	Value in other researches	References
Density at 15°C (g/cm^3)	0.9205±0.2	0.9276±0.5	0.9228	[52]
Density at 25°C (g/cm^3)	0.9182±0.07	0.9189±0.1	0.920; 0.9184	[51], [52]
Kinematic Viscosity at 40°C (mm^2/s)	27.86±0.8	28.07±0.3	30.9	[52]
Refractive Index at 25 °C	1.4776±0.003	1.4768±0.001	1.4756±0.0001	[54], [52]
Iodine Number (g I_2/100 g Oil)	112.08±0.5	110. 62±0.04	127–155, 105, 104.7±0.3	[54], [51], [52]
Acid number (mg KOH/g)	4.42±0.1	4.44±0.06	3.6 (1 to 5)	[318], [55]
Free Fatty Acids Content (wt. %)	2.22±0.1	2.23±0.3	0.2	[319]

Saponification Value (mg KOH/g Oil)	188.24±0.3	192.52±0.04	180-190, 187.8, 187.8±0.1	[54], [51], [52]
Ester value (mg KOH/g)	183.82	188.08	/	/
%glycerin	10.06	10.29	/	/
Peroxide Value, (m eq O_2/kg)	2.38±0.003	2.37±0.02	(2.38 ±0.01)	[52]

4.5.1 Evaluation of Oils Density

The oil extracted from DIC-treated Camelina seeds and from the un-textured Camelina seeds has approximately the same value and characteristics. Indeed, the values of the density of Camelina oil raw material and DIC treated at two different temperatures are presented in Table 4-9. At 15°C, the density of un-treated Camelina and DIC-treated Camelina was 0.9205 ± 0.2 and 0.9276 ± 0.5 g/cm^3, and at 25°C, it was 0.9182 ± 0.07 and 0.9189 ± 0.1 g/cm^3, respectively. These values were in line with those in literature [52] and [51].

Since density is related directly with chemical structure [52] and [320], the results obtained in this work confirmed that DIC treatment have no effect on the quality or chemical structure of the seeds.

4.5.2 Evaluation of Oils Kinematic Viscosity

The kinematic viscosity at (40°C) of un-textured and DIC-textured Camelina were (27.86 ± 0.8) and (28.07 ± 0.3) mm^2/s, as recorded in Table 4-9.

Although authors highlighted significant increasing in Camelina oil viscosity from 30.7 to 31.8 mm^2/s when Camelina seeds were heated at 180°C during one day [321] and [50], DIC treatment didn't imply any significant change in the value of kinematic viscosity. This means that the DIC treatment did not enhance any decomposition nor degradation for the oil. Thus, it strongly emphasizes that the DIC as a High-Temperature/ short-time heating does not affect the viscosity of the oil.

According to biodiesel standards; ASTM D 6751-09 and UNE-EN 14214, the viscosity value of oil that can be used as a fuel in internal combustion engines is 1.9- 6 and 3.5 - 5 mm^2/s at 40°C, respectively [322]. Therefore, it is necessary to modify the oil properties to obtain low viscosity biofuel suitable in diesel internal combustion engines.

4.5.3 Evaluation of Oils Refractive Index

Refractive index (RI) of oil is one of the most crucial quality attributes imply deception or reveal purity of oil [323]. RI is a parameter that relates to molecular weight, FA chain length, degree of unsaturation, and degree of conjugation [54].

Refractive Index RI of camelina oils investigated in the current work measured at 25 °C were (1.4776 ± 0.003) and (1.4768 ± 0.001) for oil extracted from un-textured and DIC- textured Camelina seeds respectively. These values are comparable with those from other researches as shown in the Table 4-9. It is worth noting that the refractive index increases with additional double bonds, and particularly conjugated double bonds.

The comparable RI values obtained proves that DIC treatment did not affect the structural characteristics of Camelina oil.

Usually, Refractive Index RI varies with density and/or temperature, thus sometimes predetermined curves of RI at constant temperature are used to estimate iodine number IN. The mathematical relationship between RI and IN has been described as following equation [324] and [54]:

$$\mathrm{RI\ at\ 25°C} = 1.45765 + 0.0001164\ \mathrm{IN} \qquad \textit{Eq. 4-5}$$

4.5.4 Evaluation of Oils Iodine Number

The iodine number IN or iodine value is a measure of the unsaturation degree of an oil. Iodine Number is an important parameter in studying oxidative rancidity of oils since the higher the unsaturation degree, the greater the possibility of the oils to go rancid [325].

Low iodine values lead to greater oxidative storage stability. During storage, the chemical changes and oxidative of oils are characterized by a decrease in the total unsaturation degree of oils and an increase in free fatty acid contents [321].

The data in Table 4-9 for iodine values indicated that the iodine value for the un-texture and DIC-textured Camelina were 112.08 ± 0.5 and 110. 62 ± 0.04 g I_2/100 g oil, respectively. The obtained results highly confirmed that DIC technique have no effect on the chemical composition of the seeds or its quality.

4.5.5 Free Fatty Acid and Acid Value for Oil

Free acids are frequently expressed in terms of acid value. The acid value is defined as a number of milligrams of KOH necessary to neutralize (1.0 g) of the sample [326]. The fatty acid composition of the oil in seeds have an important role in determining the functional properties, nutritional value, shelf-life, and flavor of the food products derived from them [327].

In this study Camelina oils extracted from un-textured and DIC-treated seeds showed acid values of 4.42 ± 0.1 and 4.44 ± 0.06, respectively.

The degree of free fatty acids was also determined and found to be 2.22 ± 0.1 and 2.23 ± 0.3, respectively. Although DIC-treatments exposed the seeds to high temperature 115 to 165°C, which should normally cause an increasing in FFA%, but as it is evident that DIC treatment had no effect on FFA value, because such high temperature was applied in very short time (maximum time was 45 seconds).

However, a study on Palm oil revealed that heating did not significantly affect FFA content and the percentage of free fatty acid varied from 3.500 ± 0.200 in the raw material to 3.533 ± 0.215 after the exposure to 180 °C for 14 h [328].

Another study carried out on *Camelina sativa* revealed there was no significant effects of short-time heating on Camelina oil FFA%, which varied from 3.0 for Camelina raw material to 3.25 after heating at 180°C for 24 h, and to 3.50 after 5 days [50]. The results are included in Table 4-9.

4.5.6 Evaluation of Oils Saponification Value

The saponification value SV can be defined as the quantity of potassium hydroxide (KOH) expressed in milligrams required to saponify the esters and to neutralize the free acids in 1 g of the oil [266].

The saponification value SV recorded for the un-textured and DIC-textured Camelina were (188.24 ± 0.3 and 192.52 ± 0.04) mg KOH/g Oil respectively as shown in Table 4-9.

Low refractive index and high saponification value indicate low average molecular weight of fatty acids. Saponification value was used to predict the type of glycerides in oils and fats by measured the alkali-reactive groups in the samples. Glycerides with shorter chain fatty acids have higher saponification values than those with long chain fatty acids [329].

The results obtained in this study predicted that the oil from DIC-textured seeds has very slightly higher SV (by 4.28 mg KOH/g oil) compared to the oil from un-textured seeds, this very low difference could be ignored. Also The values obtained were in line with those found in literature [54], [52] and [51].

The results confirmed that there is no significant differences in fatty acids chain lengths of Camelina oil or molecular weight after DIC treatment.

4.5.7 Evaluation of Oils Ester Value and Percentage of Glycerol

Since oils contain a certain percentage of free fatty acidity which also gets saponified during determination of the saponification value, it is necessary to exclude the saponification value contributed by the free fatty acids. This is achieved by subtract the KOH equivalent of the free fatty acidity from the saponification value of the oil. The result is called ester value corresponding to the pure triglyceride free from free fatty acids [275].

Thus ester value is defined as measurement of the saponifiable amount of glyceride present in a sample of oil [330]. The ester value was calculated and recorded for the un-textured and DIC- textured Camelina seeds. The values were 183.82 and 188.08 mg KOH/g oil respectively as shown in the Table 4-9.

Since 168.0 mg KOH/g ester value generates 92.0 mg glycerin [275]. The percentage of glycerol was also calculated for oil from the un-textured and DIC- textured Camelina. Percentage of glycerol were found to be 10.06 and 10.29 respectively.

The results obtained revealed that the amount of glyceride which saponified and the percentages of Glycerol existed in the un-textured and DIC-textured Camelina seeds oil are approximate.

It is worth mentioning that the % Glycerol is valid if the oil contains mainly triglycerides. If the oil contains mono or diglycerides, the glycerol content as determined from ester value would not be accurate [275].

4.5.8 Evaluation of Oils Peroxide Value

Peroxide value is used as a measure of the range where rancidity reactions happen during storage. It could be used as a significance of the quality and stability of oils. The oil peroxide value was also found to increase with the storage time, temperature and contact with air [321].

The peroxide value can be defined as the amount of peroxide contained in 1000 g of the substance expressed by the number of mill-equivalents of active oxygen [331].

Peroxide value measures primary oxidation reactions of the oil, which mainly take place from hydro-peroxides. In general, the lower the peroxide value, the better the quality of the oil. Oils with significant levels of peroxides may still be odorless if secondary oxidation has not begun [332]. The secondary stage of oxidation happens when the hydro-peroxides decompose to form carbonyls and other compounds in particular aldehydes. These quality aspects measured by the acid value which are the reason of the oil to get a rancid smell [333]. Peroxide value for oil from un-textured and DIC-textured seeds were (2.38 ± 0.003) and (2.37 ± 0.02) respectively as shown in the Table 4-9 , were these two results very close to each other.

All the results cited in above, confirmed that there is no change in the seeds structure when the seeds exposed to the DIC treatment. Therefore, the conclusion could be drawn from all the above results is that instant controlled pressure drop is an efficient technology for enhancing the oil yield without affecting the quality or chemical compositions of the Camelina raw seeds. The situation is confirmed throughout many previous studies using DIC as pretreatment step in extraction oils from natural products [334], [178], [143] and [335].

4.6 Fatty Acid Profiles

The most common fatty acids found in oilseeds are palmitic, stearic, oleic, linoleic and linolenic acids [336]. Those fatty acids were identified in Camelina samples investigated in the current work using GC-FID. The fatty acids identified were: saturated fatty acids (SFA): palmitic acid (C16:0) and stearic acid (C18:0), unsaturated fatty acids (USFA) including monounsaturated fatty acids (MUFA): oleic acid (C18:1) and polyunsaturated fatty acids (PUFA) such as: linoleic acid (C18:2) and linolenic acid (C18:3).

Figure 4-7 shows GC-FID Chromatogram of the standard sample of Fatty Acid Methyl Esters which consist of: Methyl esters of; methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate. Figure 4-8 and Figure 4-9 shows GC-FID Chromatogram of the FAMEs produced from un- textured Camelina seeds and DIC-textured Camelina seeds respectively by transesterification.

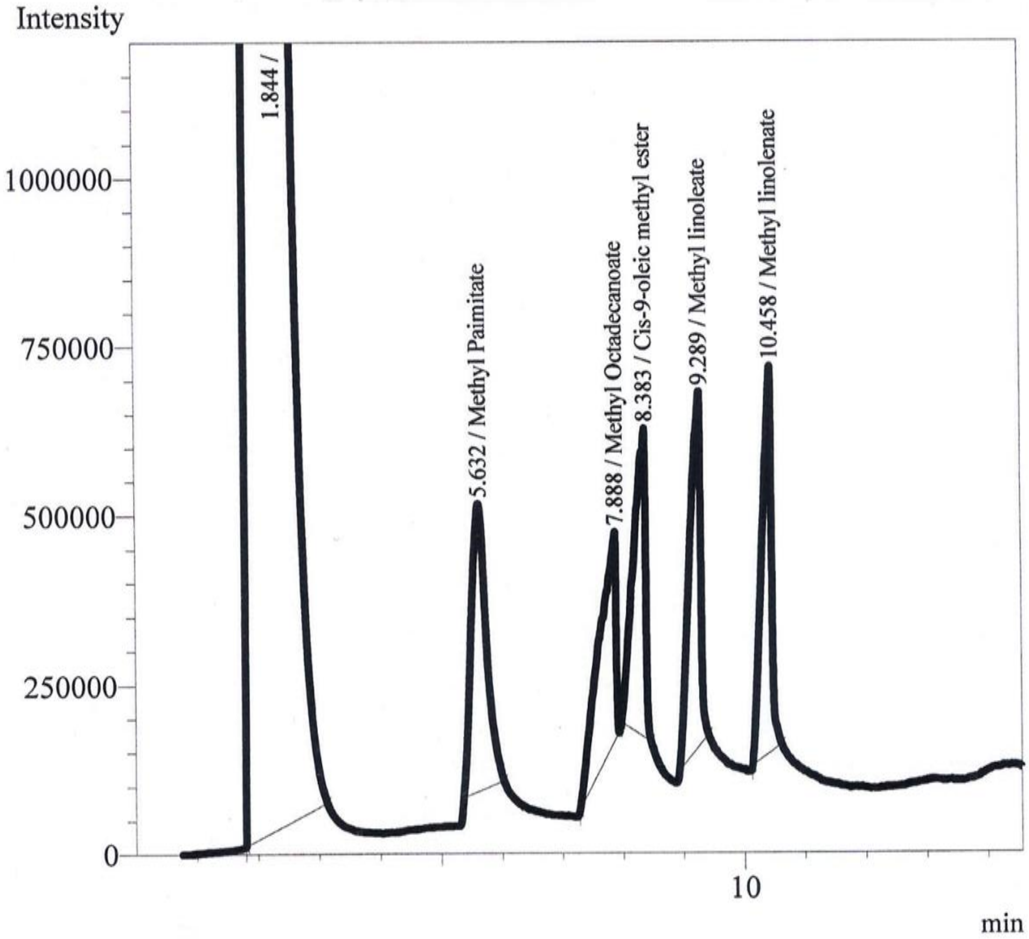


Figure 4-7. GC-FID Chromatogram of Fatty Acid Methyl Esters (FAMEs) Standard: Methyl esters of; methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate.

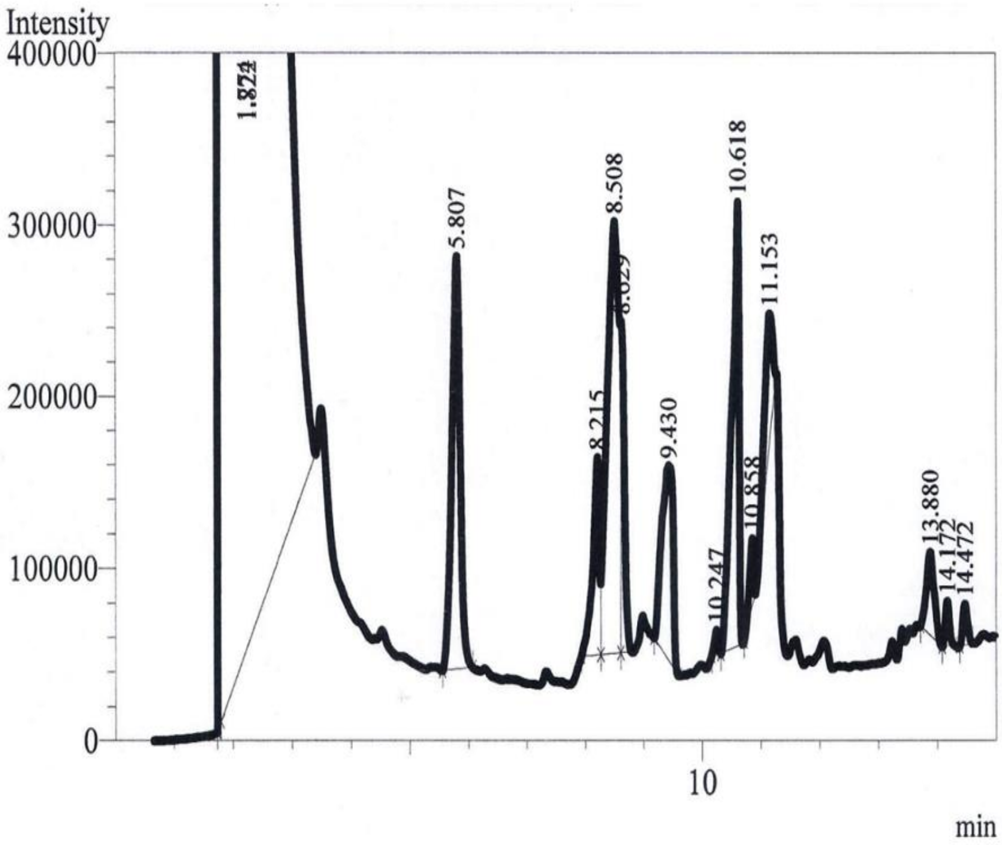


Figure 4-8. GC-FID Chromatogram of FAMES produced from un-textured Camelina by transesterification

Since Figure 4-8 represents the FAMEs produced from transesterification of the oil extracted from the un-texture Camelina seeds, the parent oil composition could be identified by comparing the GC-FID chromatograms of Figure 4-7 and Figure 4-8. The results are shown in Table 4-10.

Table 4-10. The main fatty acids composed in oil from un-textured Camelina *seeds*

Ret. Time mint	FAMEs	Fatty Acids	Fatty Acids wt. %
5.807	Methyl Palmitate	Palmitic acid	16.50
8.215	Methyl Stearate	Stearic acid	6.15
8.508	Methyl Oleate	Oleic acid	32.50
9.430	Methyl Linoleate	Linoleic acid	13.54
10.618	Methyl Linolenate	Linolenic acid	21.83

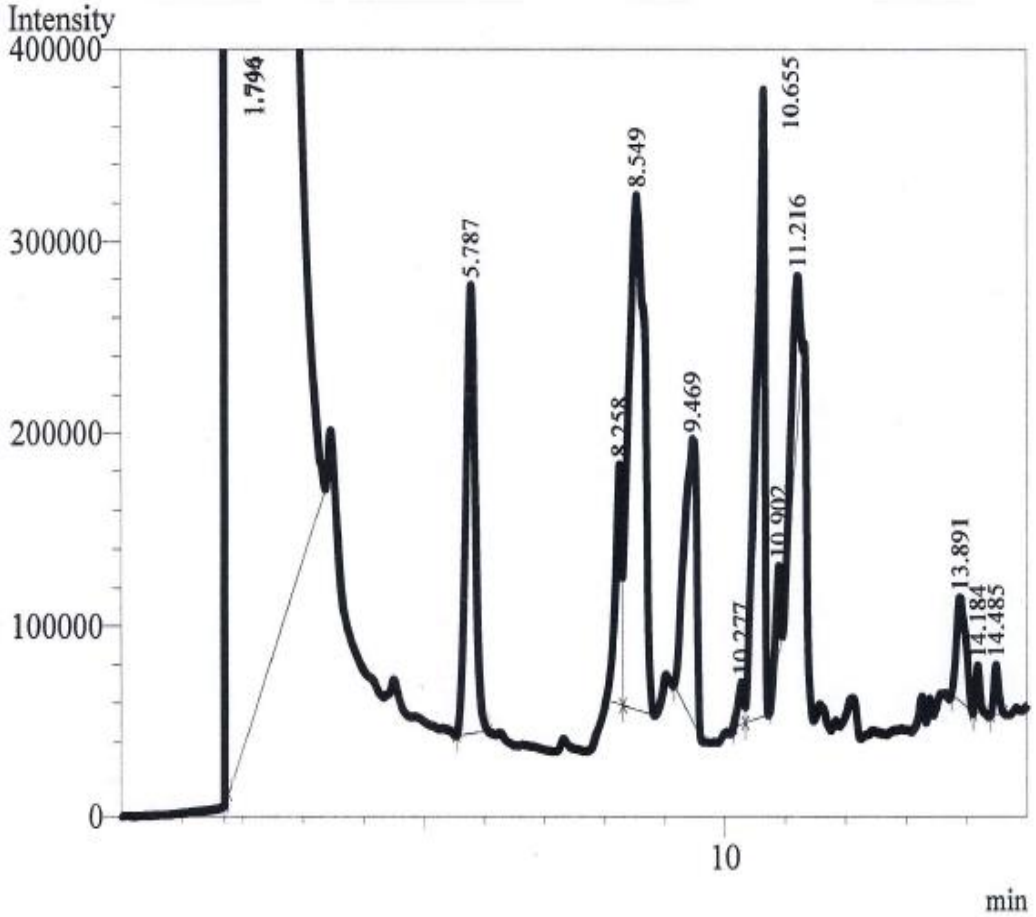


Figure 4-9. GC-FID Chromatogram of FAMES produced from DIC-textured Camelina seeds by transesterification

Since Figure 4-9 represents the FAMEs produced from transesterification of the oil extracted from the DIC-textured Camelina seeds by pressing (sample of experiment no. 5, DIC treated at Temp. 157.7 °C, time 40s), the parent oil composition could be identified by comparing the GC-FID chromatograms of Figure 4-7 and Figure 4-9. The results are recorded in Table 4-11.

Table 4-11. The main fatty acids composed in oil from DIC textured Camelina *seeds*

Ret. Time mint	FAMEs	Fatty acids	FA. wt. %
5.787	Methyl palmitate	Palmitic acid	17.70%
8.258	Methyl stearate	Stearic acid	6.22%
8.549	Methyl oleate	Oleic acid	34.01%
9.469	Methyl linoleate	Linoleic acid	14.47%
10.655	Methyl linolenate	Linolenic acid	21.48%

From Table 4-10 and Table 4-11, the five major fatty acids found in the two Camelina oil samples were linolenic acid, linoleic acid, oleic acid, stearic acid and palmitic acid. Therefore, it is evident that the composition of the oils extracted from the un-textured and DIC-textured Camelina seeds were similar revealing that there was no change in Camelina oil composition when it is exposed to DIC thermo-mechanical treatment.

Most of the researches carried out on identification of fatty acids of Camelina seeds, revealed that polyunsaturated fatty acids (linoleic and linolenic acid) form the major content among the fatty acids present [78], [60] and [337].

Conversely, the current work demonstrated that the monounsaturated; oleic acid form the major content followed by the polyunsaturated fatty acids, linoleic acid and linolenic acid. Similar results were reported in master thesis conducted by *Sampath* [51], who characterized 18 types of Camelina oils. The author found that just one of the 18 types contained oleic acids as a major fatty acid in Camelina oil. The variations in fatty acids content has been interpreted due to the changing in growing location, such as; type of soil, climate, and nutritional factors [51].

4.7 Transesterification

4.7.1 RSM Modeling and Optimization of Transesterification of the Oil from Fresh (Un-textured) Camelina Seeds

Response Surface Modeling (RSM was carried out for each response variable in order to test the model significance and suitability and to optimize the operating variables. The significances of all terms in the second-degree polynomial equation were statistically analyzed through Pareto charts based on ANOVA value. The model is analyzed using the lack-of fit test, and coefficient of determination (R^2). The larger the value of R^2 (up to 1) reveals that the model is more adequate to the experimental results.

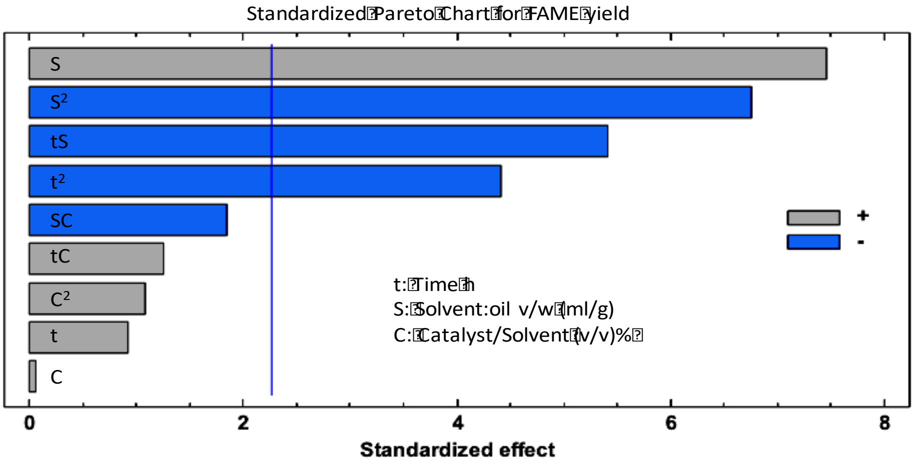
The RSM results of transesterification of the oil from fresh (un-textured) Camelina seeds based on the experimental data recorded in Table 4-12 were analyzed by RSM software and plotted in Figure 4-10; Pareto-charts, Main effects plot, Interaction Plot, Contours of estimated surface and response surface.

Table 4-12. Central composite design of TE for the raw Camelina seeds oil; the actual values of the independent variables and the FAMEs as responses

Trial No.	t (Time h)	S (Solvent:oil v/w) (ml/g)	C Catalyst/Solvent (v/v)%	Y (TE-FAMEs : g FAMEs/g db)
15-19	3.75	10:1	4	0.80±0.003
1	3.75	17:1	4	0.6536
2	3.75	10:1	6	0.9344
3	7	10:1	4	0.6698
4	3.75	3:1	4	0.1084
5	3.75	10:1	2	0.9259
6	0.5	10:1	4	0.4355
7	1.85	14:1	5.1	0.8661
8	1.85	14:1	2.9	0.9592
9	1.85	6:1	2.9	0.2063
10	5.68	6:1	2.9	0.3475
11	5.68	6:1	5.1	0.6495
12	5.68	14:1	5.1	0.4774
13	5.68	14:1	2.9	0.6186
14	1.85	6:1	5.1	0.1395

The estimated mathematical model was expressed in the polynomial multiple linear regression model (p-value <0.05) showing the effect of the transesterification conditions on biodiesel yield is shown in Eq. 4-6.

The vertical line on Pareto chart corresponds to the value of ANOVA (here 0.05) and determines the effects that are statistically significant. The standardized effect is the estimated effect divided by its standard error. Hence a low standardized effect can mean either a low effect of the parameter or a large experimental error [338].



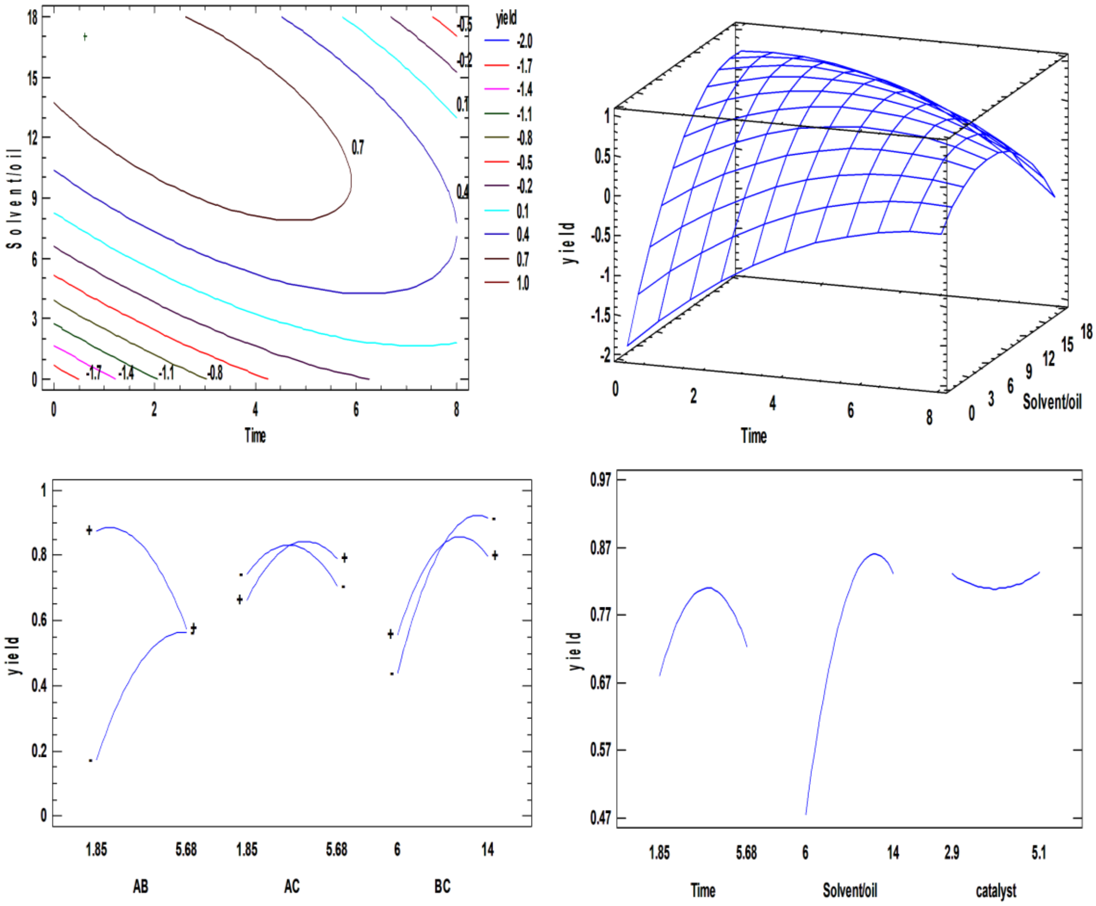


Figure 4-10. Pareto-charts, Main effects plot, Interaction Plot, Contours of Estimated Surface, and response surface of the effects of solvent/ oil ratio, time of reaction and catalyst concentration on biodiesel yield

$$\text{Biodiesel yield} = -1.858 + 0.38021t + 0.377S - 0.0907C - 0.02916t^2 - 0.0225tS + 0.0190tC - 0.0097S^2 - 0.01334SC + 0.0192C^2 \qquad \text{Eq. 4-6}$$

Where A is the time, B is solvent/oil (v/v) and C is catalyst concentration (v/v) %. The fit of the model was checked with the coefficient of determination R^2, which was found to be 0.9456 with an adjusted R^2 (adjusted for d.f.) = 89.12%, indicating that the model could explain experimental results.

Figure 4-10 shows the effects of the operating parameters in terms of biodiesel yield (g FAMEs/g dry basis (db)). Pareto chart of standardized effects was plotted in order to show significant effects of all variables (linear, quadratic and interactions between variables). The vertical line represents the limit between the significant and insignificant effects regarding the response. The length of each parameter characterizes the absolute importance of the estimated effects. Moreover, the color of the squares indicates whether the effect is positive or negative [143].

Response Surface Modeling (RSM plots illustrated in Figure 4-10 issued from Table 4-12) predicted that the studied parameters had a significant effect on FAMEs yield (p-value <0.05) as well as the interactions between the parameters.

For instance, the squares of the factor B: solvent/oil (v/v), and the positive sign of the gray color indicates the significant and the positive effect of factor B on % yield of biodiesel. This finding can be easily explained considering that the increasing the solvent/oils ratio leads to increase in biodiesel conversion yield.

while (S^2) quadratic effect of solvent/oil (v/v), reaction time t with S solvent/oil (v/v) interact (tS), and quadratic t^2 reaction time parameter, were also outstripping the vertical line and is in blue color *i.e.* these parameters have significant effect but the effect was negative on oil yield.

Also, it is possible to perceive from Figure 4-10, that the catalyst percentage have no significant effect on the FAMEs yield neither as individual parameters, nor as interaction with other parameters. This result can be interpreted as follows:

At elevated temperature, there is ability to convert triglycerides into methyl esters without the aid of a catalyst [199] and [339]. However, the addition of an excessive amount of catalyst to the TE reaction increases emulsion formation. It was observed that when transesterification temperature was more than 60°C and catalyst concentrations was more than 1.5% , large amount of soaps were produced [340].

Another study demonstrated that at low temperatures, biodiesel production increases with increasing the catalyst concentration 1.7 wt. % [341]. However, there is a direct relation between the reaction temperature and amount of catalyst added to the reaction.

The highest biodiesel yield was (0.9592 g FAMEs/g db) for the oil extracted from the un-textured raw Camelina. Empirical models permitted to identify the optimal value of biodiesel yield to be 1.19714 g FAMEs/g db for the Camelina oils achieved at solvent/oil ratio = 17 ml solvent/ 1 ml (Camelina oil), while catalyst/solvent ratio = 2 %, and at reaction time equal to 0.61 h which equal to (36.6 minutes).

As it is shown in Eq. 4-6, only the linear term of time and quadratic terms of were significant and their regression coefficient had one positive coefficient values with three negative terms. This indicate that the higher the amount of solvent/oil ratio, the higher the FAMEs yield from transesterification reaction, similar findings are reported in the literature [342], [343] and [344].

The amount of alcohol in the reaction plays a vital role. Indeed, since the transesterification is an equilibrium reaction, the ratio between methanol and molar of total fatty acids used for transesterification is normally higher than the stoichiometric value to favor product formation. While, in the presence of an interaction effect, the variables cannot be analyzed separately, therefore the application of statistical methods will verify the significance of the interaction effects.

4.7.2 RSM Modeling and Optimization of Transesterification of the Oil from (DIC-textured) Camelina Seeds

Transesterification reaction conditions estimated from the RSM analysis of the raw material were applied to study the TE reactions carried out for (13 samples) of oil produced from pressing of DIC-textured seeds. The experimental results of FAMEs yield are listed in Table 4-13.

Table 4-13. Central composite design of TE for the DIC-textured Camelina *seeds oil; the actual values of the independent variables and the FAMEs as responses*

Trial No.	**Treatment Temperature (Saturated steam pressure P)**	**Processing time t (s)**	**Yield of FAMEs (g /g oil db)**	
			Observed Value	Fitted Value
Control	/	/	0.9649	/
Central point	140 °C (0.36 MPa)	30	0.98±0.01	0.9750
DIC 2	165 °C (0.7 MPa)	30	0.9991	0.9916
DIC 3	140 °C (0.36 MPa)	45	0.9743	0.9800
DIC 5	157.7°C (0.58 MPa)	40.6	0.9981	1.0012
DIC 6	157.7°C (0.58 MPa)	19.4	0.9478	0.9528
DIC 8	122.3°C (0.21 MPa)	19.4	0.9977	0.9865
DIC 9	122.3°C (0.21 MPa)	40.6	0.9948	0.9817
DIC 11	115°C (0.17 MPa)	30	0.9862	1.0017
DIC 12	140°C (0.36 MPa)	15	0.9474	0.9503

Central-point: DIC (1, 4, 7, 10, 13)

DIC-textured Camelina seeds oil were processed under the conditions previously optimized with the TE of oil extracted from the un-textured raw material. Table 4-13 shows the FAMEs yield from TE for oil which was produced by pressing the un-textured seeds and DIC-textured seeds were to be 0.9649 and 0.9981 g FAMEs/ g oil db respectively. The TE experimental results are plotted in Figure 4-11.

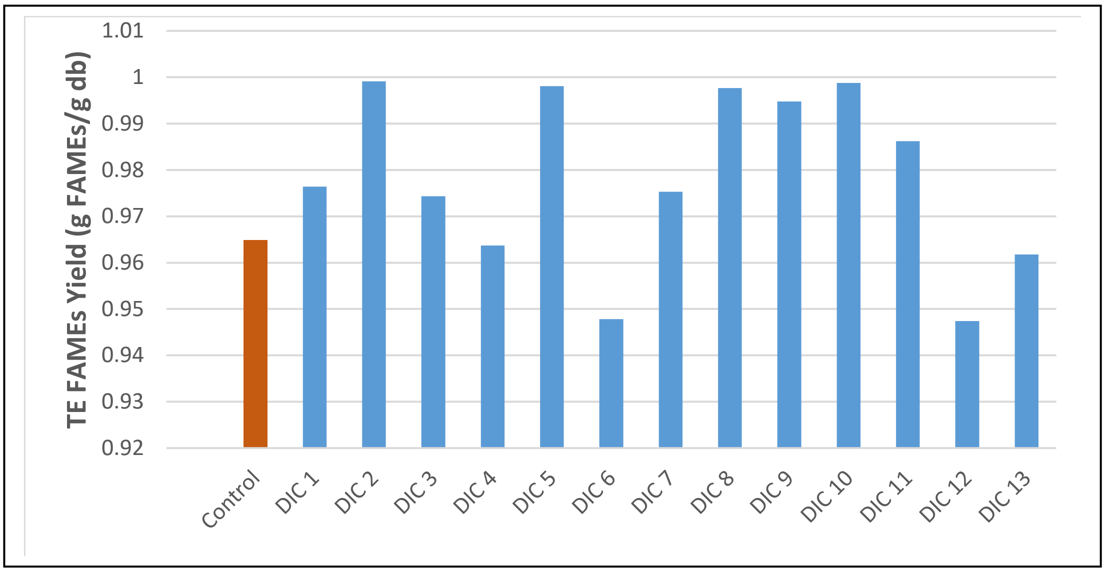


Figure 4-11. TE biodiesel yield for the raw un-textured (Conventional TE process: in red) and (innovative DIC/ISTE process: in blue) from Camelina seeds oil

It is worth noting that the oil which has been produced from the un-textured and all the DIC treated seeds had approximately the same quantity yield of FAMEs which confirm there were no different in chemical composition between the oil extracted from DIC-textured and the un-textured seeds.

However, DIC technique had an effect on the amount of oil which extracted from seeds probably thanks to the higher availability of oil within the more porous materials. Indeed, since DIC allows very high rate of auto-vaporized volatile compounds such as water, it would imply very effective swelling or even rupture of cell walls. The impact of such a porous structure is to increase the extraction yield [176]. Therefore, the optimization of TE was just depended on the TE reaction parameters.

4.8 *In-situ* Transesterification

While transesterification technique is considered costly technique due to the two-step process (oil extraction and then transesterification), implying consuming long time, and in order to overcome the above shortcomings, *in-situ* transesterification has been applied to minimize the time and to reduce the cost however it has been reported that biodiesel production via *in-situ* process was of much lower yield than that obtained via conventional process [281].

Since porosity and texturing ratio normally depends on both amount of auto-vaporized water, and rheological behavior involving glass transition of the product [345], the effect of DIC on *in-situ* transesterification depend on DIC temperature, vacuum level, and pressure-drop rate.

4.8.1 RSM Modeling and Optimization of *In-situ* Transesterification for the Fresh (un-textured) Camelina Seeds

Response Surface Modeling (RSM) was carried out to model and optimize the effect of the ISTE parameters on FAMEs yield. The experimental ISTE data were fitted to a mathematical model and the model was tested for significance and suitability. The significances of all terms in the second-degree polynomial equation were statistically analyzed through Pareto charts based on ANOVA value with p-value of 0.05. The model is analyzed using the lack-of fit test, coefficient of determination (R^2) and adjusted-R^2 analysis.

The RSM results of the experimental data listed in Table 4-14 were plotted in Figure 4-12: Pareto-charts, general trends, response surface, etc.). Expressed through out a polynomial multiple linear regression model Eq. 4-7.

Table 4-14. Central composite design of ISTE for the raw Camelina *seeds; the actual values of the independent variables and the FAMEs yield as responses*

Exp. No.	S Solvent solution: seed weight (v/w) (ml/g)	C Catalyst/Solvent (v:v)% of solvent solution	Y ISTE-FAMEs (g FAMEs/g ddb)
1, 4, 7, 10, 13	30	5.5%	0.3066±0.0005
2	50	5.5%	0.3815
3	30	10%	0.3399
5	44.1	8.7%	0.3626
6	44.1	2.3%	0.3494
8	15.9	2.3%	0.2573
9	15.9	8.7%	0.2678
11	10	5.5%	0.2414
12	30	1%	0.2793

The vertical line on Pareto chart determines the effects that are statistically significant with a p-value of 0.05. The standardized effect is the estimated effect divided by its standard error. Hence a low standardized effect can mean either a low effect of the parameter or a too large experimental range.

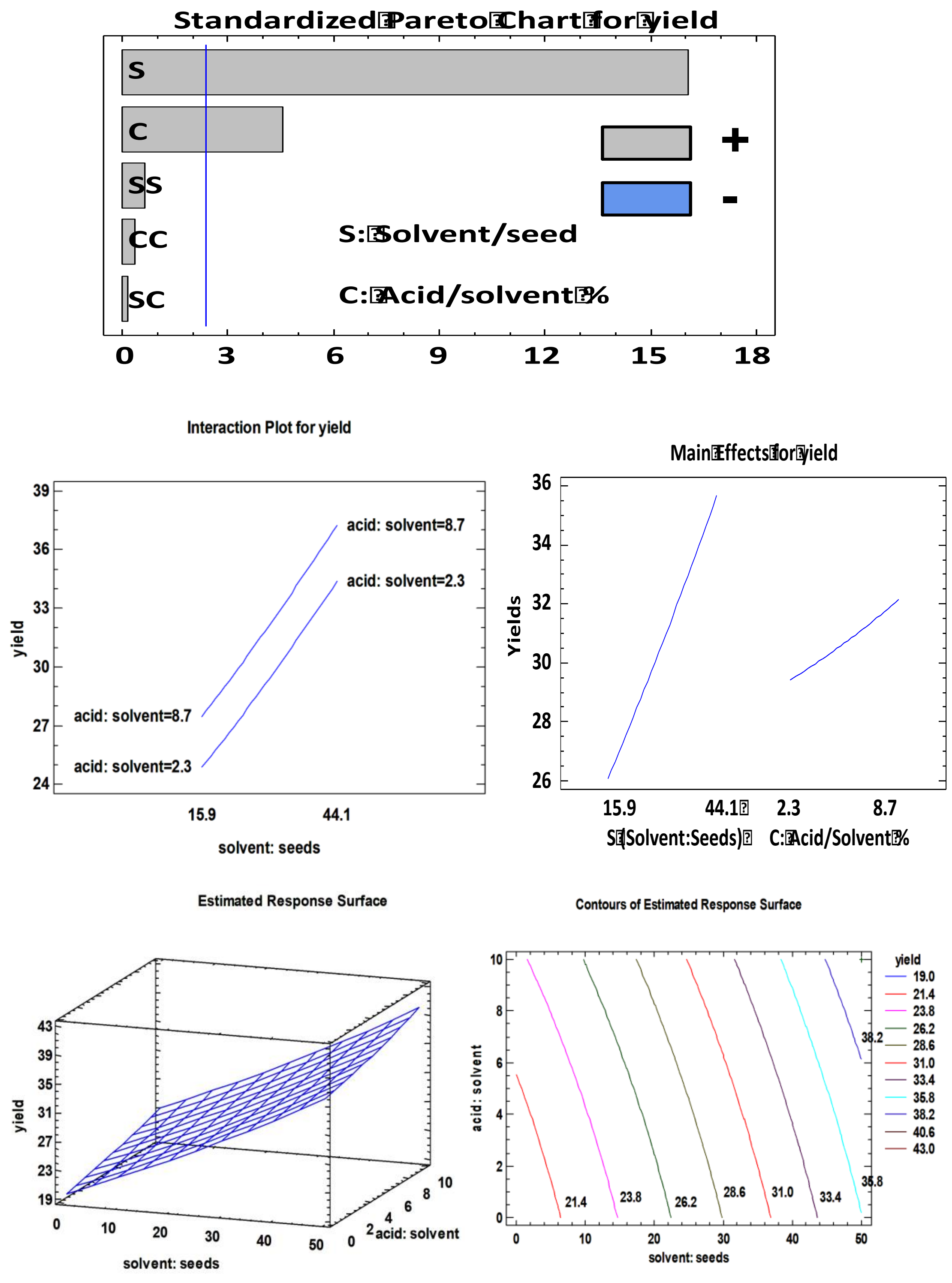


Figure 4-12. Pareto-charts, main effects plot, interaction Plot, Contours of Estimated Surface, and response surface of the effects of solvent/seeds ratio and catalyst concentration on biodiesel yield

The estimated second order polynomial model (p-value <0.05) showing the effect of the *in-situ* transesterification conditions on biodiesel yield is shown in Eq. 4-7:

$$\begin{aligned}\text{Biodiesel yield} \\ &= 19.633 + 0.2692\mathrm{S} + 0.2544\mathrm{C} + 0.00106\mathrm{S}^2 + 0.00150\mathrm{SC} \\ &+ 0.0117\mathrm{C}^2\end{aligned} \qquad \text{Eq. 4-7}$$

Where: C is the catalyst concentration (v/v) %, S is solvent/ seeds (v/w), R^2 = 97.55%, Adjusted R^2 (adjusted for d.f. = 95.80%).

Figure 4-12 shows the estimated RSM plots reflecting the effect of the ISTE operating parameters in terms of biodiesel yield (g FAMEs/g of ddb) Camelina seeds. It is well noticed that both independent variables were significant. However, S (solvent/seeds ratio) had the most significant impact. This finding can be easily explained considering that increasing the solvent/seeds ratio would enhance the interaction between the reactants whatever the porosity, diffusivity and lipid availability in the raw material are, thus increasing the reaction kinetics and the biodiesel conversion yield. As shown in Eq. 4-7, only the linear terms were significant and their regression coefficients had positive coefficient values. This indicates that the higher the amount of solvent/seed ratio and the acid catalyst concentration, the higher the FAMEs yield. Similar findings were reported in the literature [346], [45], [244], [220] and [43].

The amount of alcohol in the reaction plays a vital role. Indeed, since the transesterification is an equilibrium reaction, the molar ratio of methanol to total fatty acids used for ISTE is normally higher than the stoichiometric value to favor product formation. The highest experimental value of biodiesel yield for the un-textured raw Camelina was 0.3815 g FAMEs/g ddb. The empirical model estimated from RSM permitted to identify the optimal value of biodiesel yield to be 0.395355 g FAMEs/g of ddb Camelina seeds achieved at S (solvent/seed ratio) = 50 ml solvent/g of Camelina seeds, and C (catalyst/solvent ratio) = 10 %.

4.8.2 RSM Modeling and Optimization of FAMEs Yield of the DIC-assisted *In-situ* Transesterification of Camelina Seeds

The optimized *in-situ* transesterification reaction conditions estimated from the RSM analysis of the raw seeds were applied to study the impact of DIC process on FAMEs yield throughout ISTE of 13 DIC-textured samples Table 4-15.

Table 4-15. Central composite design of ISTE for the DIC-textured Camelina *seeds; the actual values of the independent variables and the FAMEs yield as responses*

No.	**Treatment Temperature T (°C)**	**Processing time t (s)**	**Saturated steam pressure (MPa)**	**ISTE FAMEs Yield (g FAMEs/g seeds ddb)**	
				Observed values	Fitted values
Control	/	/	/	0.3935	/
DIC Central points	140	30	0.36	0.6592 ± 0.0098	0.6592
DIC 2	165	30	0.7	0.6056	0.6662
DIC3	140	45	0.36	0.5859	0.6369
DIC5	157.7	40.6	0.58	0.7731	0.7081
DIC6	157.7	19.4	0.58	0.6083	0.5680
DIC8	122.3	19.4	0.21	0.5742	0.5719
DIC9	122.3	40.6	0.21	0.5926	0.5657
DIC11	115	30	0.17	0.5616	0.5684
DIC12	140	15	0.36	0.5260	0.5422

DIC Central points: DIC 1,4,7,10,13

The ISTE experimental results are plotted in Figure 4-13. It is worth mentioning that all the DIC treated samples had higher FAMEs yield compared to the un-textured raw material.

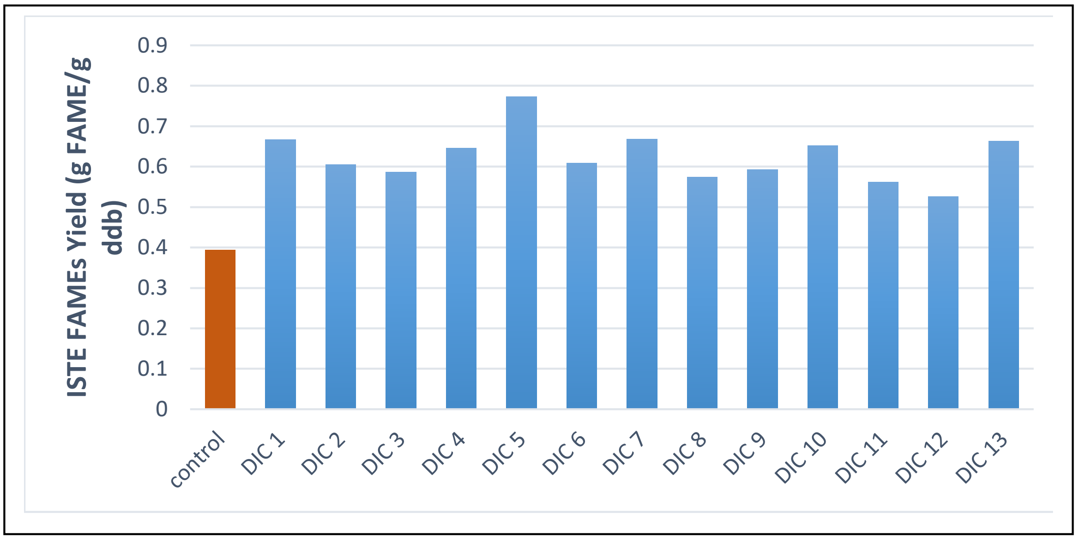


Figure 4-13. ISTE biodiesel yield for the raw un-textured (Conventional ISTE process: in red) and (innovative DIC/ISTE process: in blue) from Camelina seeds

A significant increase in FAMEs yield was observed for sample no. 5 (DIC-textured at 157.7°C for 40.6 s) which had approximately twice more FAMEs yield (0.7731 g FAMEs/g ddb seeds) compared to (0.3935 g FAMEs/g ddb seeds) from the un-textured raw material.

To analyze the experimental data, statgraphic method was exploited. The estimated effects and interactions can be reflected by p-values, which allowed DIC operating variables; treatment time, t and temperature, T to get significant impacts on FAMEs yield, for p-value < 0.07.

F-Ratio and P-Value estimated from ANOVA corresponded to DIC operating variables are listed in Table 4-16.

Table 4-16. ANOVA data of ISTE FAMEs yields Y (dependent variable) versus various terms of independent parameters of DIC temperature T and time t

Source	DIC Treatment Time, t	DIC Treatment Temperature, T	t^2	tT	T^2
F-Ratio	4.64	4.95	4.36	2.77	1.58
P-Value	0.0683	0.0614	0.0751	0.1401	0.2491

The standard error of the fitted values shows 0.0440 as a standard deviation of the residuals, while the average value of the residuals is revealed by 0.02386 as the mean absolute error (MAE).

To plot the estimation of importance, Pareto Charts Figure 4-14 reveals the statistical significance of the effects; however, the estimated P-value was greater than 5.0 %, revealing that there is no indication of serial autocorrelation in the residuals at the 5.0% significance level. Accordingly, the DIC processing variables within the range applied in the current work seemed not significant, however the estimated regression factor R^2 equaled 71.7% and adjusted R^2 was limited to 51.4%. The polynomial second order equation showing the effect of DIC operating variables on FAMEs yield is shown in Eq. 4-8.

$$\mathrm{Y} = -0.4831 - 0{,}0056\mathrm{t} + 0{,}0148\mathrm{T} - 0{,}0003\mathrm{t}^2 + 0{,}0002\mathrm{tT} - 0{,}00007\mathrm{T}^2 \qquad \textit{Eq. 4-8}$$

Where: T is the DIC processing Temperature (°C), t is the DIC treatment time (s), and Y is FAMEs yield (g FAMEs/g db).

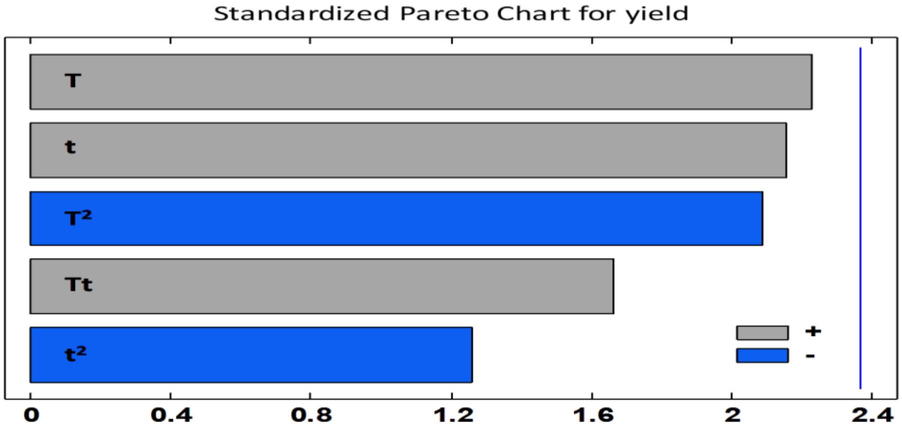


Figure 4-14. Standardized Pareto Chart (p-value=5%) of the processing temperature T and the processing time t for FAMES yield produced by ISTE of DIC textured Camelina seeds

The highest FAMEs yield was estimated to be $Y_{optimized}$ = 0.72 g FAMEs/g ddb correlated with DIC-textured Camelina seeds at a treatment time $t_{optimized}$ = 43 s and a processing temperature $T_{optimized}$ =165 °C.

The contour plots Figure 4-15 clarify the situation. These optimized DIC conditions allowed the extensive yield of biodiesel to be so moderate resulted in a convenient, high performance and cost-effective *in-situ* transesterification manufacturing process.

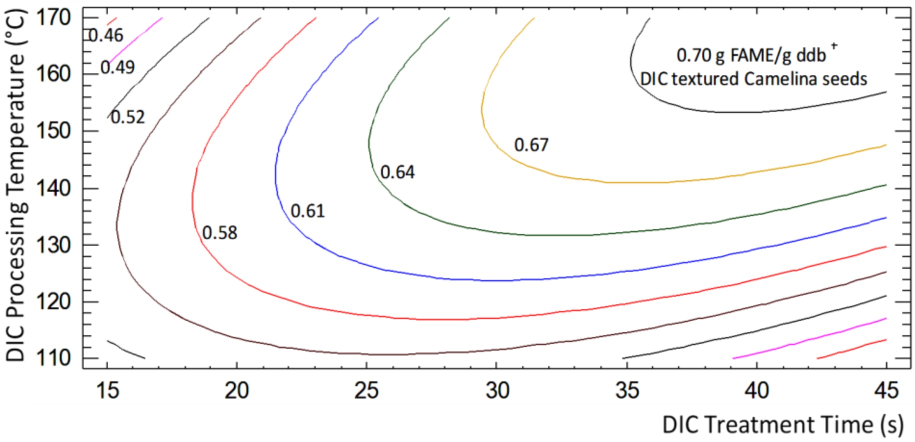


Figure 4-15. Contours of estimated response surfaces of the effects of DIC processing temperature, T and processing time, t on FAMEs yield from DIC textured Camelina seeds

4.9 Assessment for the Impact of DIC on FAMEs Quantity Produced by ISTE

Characterization of FAMEs produced by transesterification of the oils extracted from raw un-textured and DIC-textured seeds was carried out successfully by GC-FID to identify qualitatively and quantitatively the main fatty acids and the corresponding

FAMEs of Camelina seeds. FAMEs produced by ISTE from raw un-textured and DIC-textured Camelina seeds were also identified by GC-FID.

This was performed by testing the FAMEs produced by ISTE for different reaction time (30, 60 and 120 minutes) using the same program used for FAMEs produced by TE. Table 4-17 and Table 4-18, and Figure 4-16 and Figure 4-17 show the estimated results.

Table 4-17. Composition and weight percent for FAMEs produced from un-textured Camelina *seeds by ISTE at different reaction time*

Reaction Time (min.)	Methyl Palmitate wt.%	Methyl Stearate wt.%	Methyl Oleate wt.%	Methyl Linoleate wt.%	Methyl Linolenate wt.%
30	6.46%	7.76%	10.97%	1.98%	0.56%
60	7.18%	10.94%	21.98%	4.14%	1.85%
120	8.22%	12.15%	22.61%	6.82%	1.96%

Table 4-18.Composition and weight percent for FAMEs produced from DIC-textured Camelina *seeds by ISTE at different reaction time*

Reaction time min. DIC	methyl Palmitate wt.%	methyl Stearate wt.%	methyl Oleate wt.%	methyl Linoleate wt.%	methyl Linolenate wt.%
30	4.99%	5.31%	16.50%	2.10%	0.56%
60	9.09%	11.58%	21.48%	5.39%	1.15%
120	9.49%	14.85%	28.34%	7.21%	2.38%

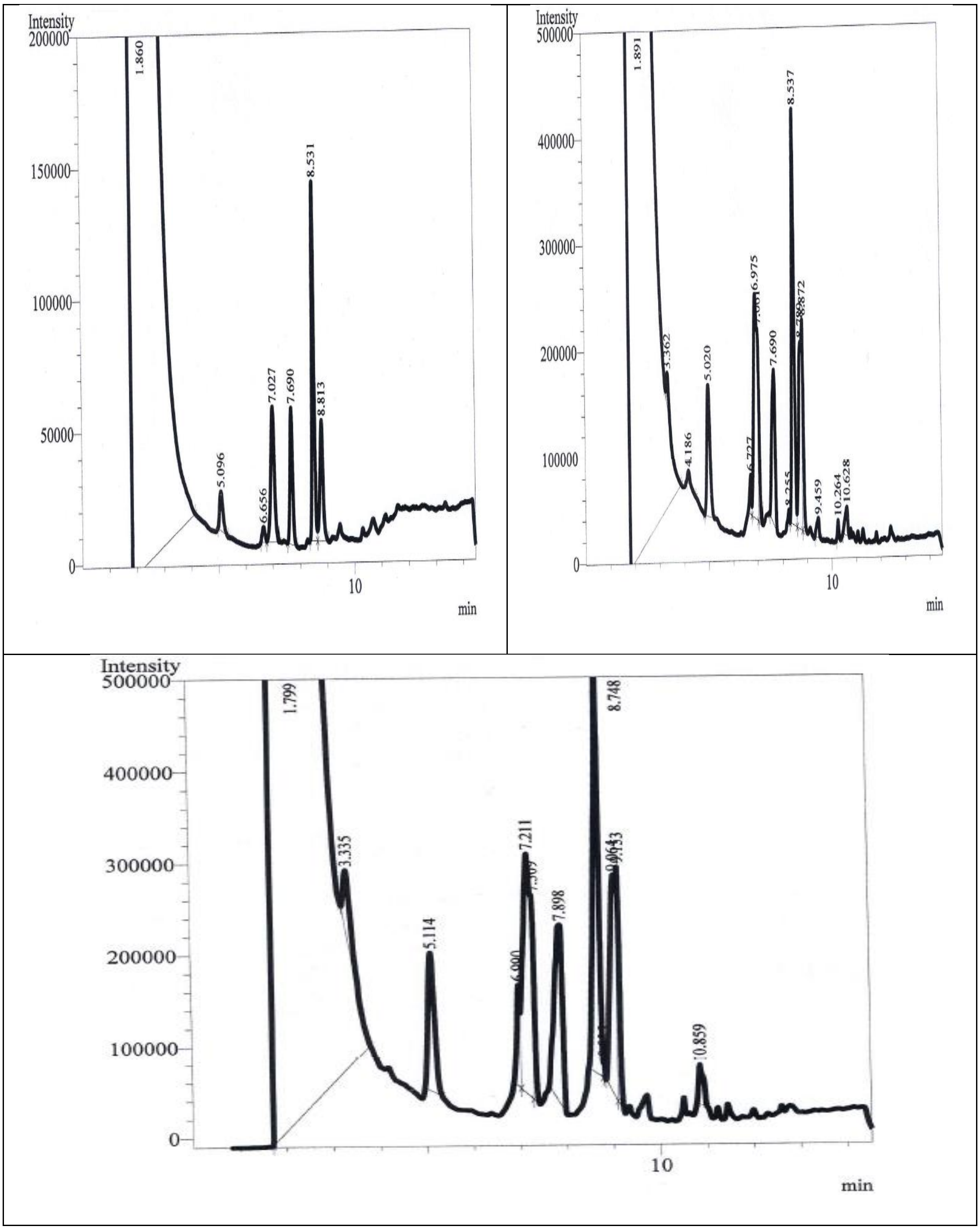


Figure 4-16. GC-FID chromatogram of ISTE-FAMEs (un-textured Camelina seeds after 30, 60, and 120 min, respectively)

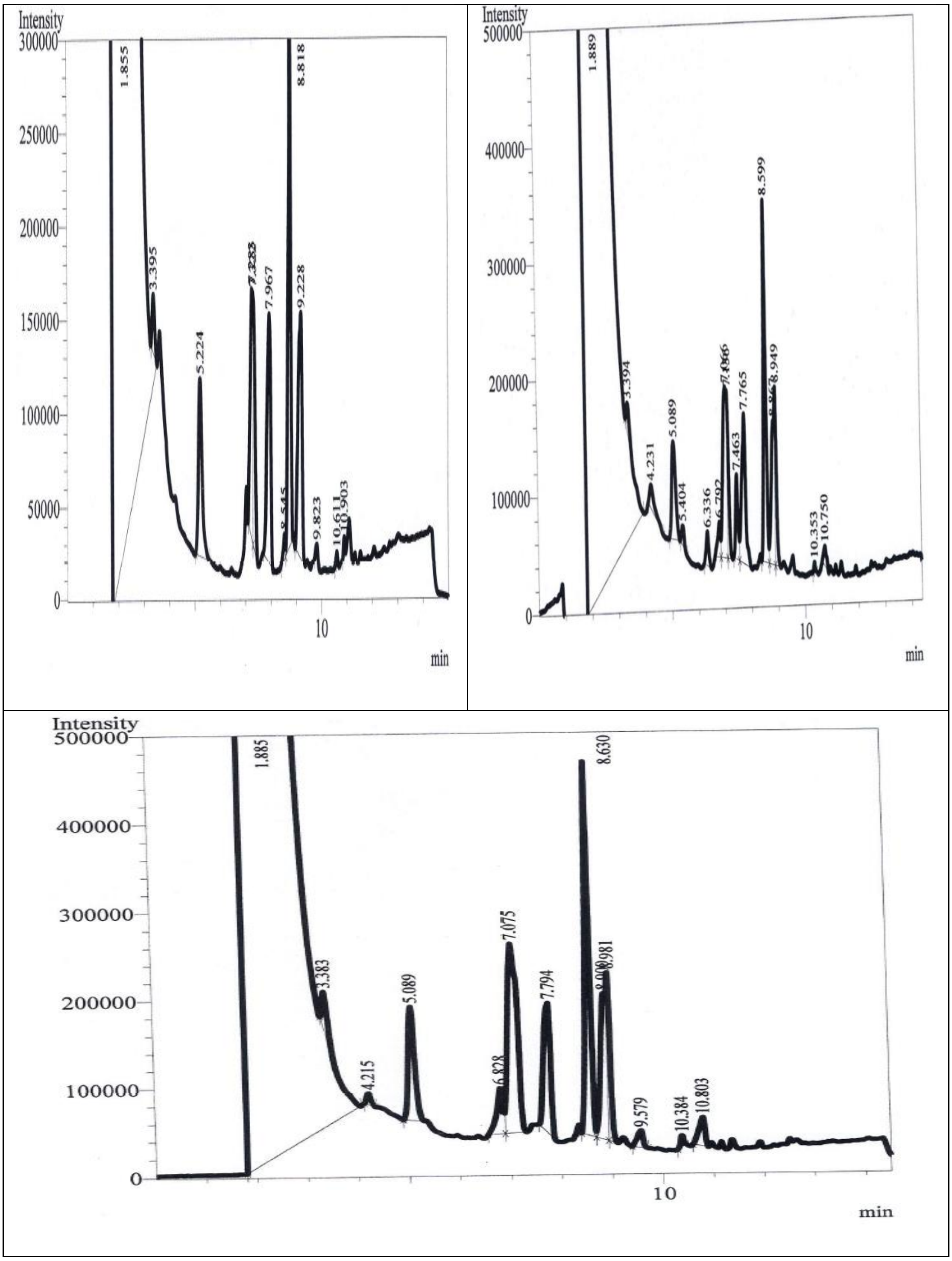


Figure 4-17. GC-FID chromatogram of ISTE-FAMEs (DIC-textured Camelina seeds at 30, 60, and 120 min, respectively)

It is obvious to note that DIC pretreatment enhances the weight percent of the different esters including the composition of FAMEs compared to those produced from untreated seeds. However, lower yield of FAMEs produced by the ISTE was detected comparing to those produced by TE, Table 4-18 shows these comparison results.

Table 4-19. Comparison between the FAMEs yields in weight percent from TE and ISTE processes

FAMEs	**TE FAMEs Wt. % after 36.6 min**	**DIC /TE FAMEs Wt. % after 36.6 min**	**ISTE FAMEs Wt. % after 30 min**	**DIC/ISTE FAMEs Wt. % after 30 min**
Methyl Palmitate	**16.5**	17.7	6.46	4.99
Methyl Stearate	**6.15**	6.22	7.76	5.31
Methyl Oleate	**32.5**	34.01	10.97	16.5
Methyl Linoleate	**13.54**	14.47	1.98	2.1
Methyl Linolenate	**21.83**	21.48	0.56	0.56
SUM:	90.52	93.88	27.73	29.46

4.10 Evaluation of Fuel Properties of Camelina Biodiesel

Table 4-20 summarized the properties of biodiesel produced from Camelina seeds oil and Camelina seeds by TE and ISTE respectively. The used seeds were DIC-textured seeds expanded at 157.7 ˚C (Saturated steam pressure of 0.58 MPa) for 40.6 s (experimental number 5). Table 4-20 included also the standards specified in the ASTM D6751 and EN 14214 as well as the published values in literature. It is obvious that the DIC texturing Camelina seeds improves the biodiesel yields without any modification of the properties.

Table 4-20. Properties of Camelina *biodiesel with the standards specified in the ASTM D6751 and EN 14214 as well as published values in literature*

Properties	**Other research values**	**Test method**	**TE-FAMEs**	**ISTE-FAMEs**	**Test method used in current study**	**ASTM D 6751-09**	**UNE-EN 14214**
Density g /ml at 15 ˚C	0.91 [220], 0.888 [85], 0.887 [300]	EN ISO 12185	0.882±0.7	0.886±0.2	EN ISO 12185	-	0.860-0.900
Specific gravity	0.87-0.88 [91]		0.887	0.881			
API gravity			28.02	29.11			
Kinematic viscosity at 40°C cSt	4.3 [85], 4.15 [318], 2.9 to 3.15 [91], 3.9 [300]	ASTM D 445	4.13±0.01	3.58±0.03	ASTM D 445	1.9-6	3.5-5
Dynamic viscosity cP (mPa.s)			3.64	3.17			
Acid value (mg KOH /g)	0.76 [220], 0.31 [318], 0.43 [347], 0.25 [300], 0.15 [85]	EN 14104	0.38±0.04	0.33±0.1	EN 14104	≤ 0.50	≤ 0.50
Iodine value (g I_2 /g)	152 [85], 151 [318], 156 [347], 166.2 [300]	EN 14111	142±0.7	145±0.03	EN 14111	-	≤ 120
Cetane number	49.26 to 51.17 [91], 49.7 [300]	EN 15195	54.8±0.5	53.6±0.2	ASTM E1655	≥ 47	≥ 51
Carbon residue Wt.%	0.019 (100%sample) [85], 0.003 [300]	EN ISO 3679	0.016±0.3	0.052±0.01	D 189	≤ 0.05 (100% sample)	≤ 0.3 (on 10% distillation residue)
Cloud point °C	0 [85], 3 [318], 7 [347], -1.6 [300]	ASTM D 2500	-1 ±0.04	0±0.02	ASTM D 2500	Accor-ding to climate zone	
Pour point °C	-4 [318], -11 to -8 [91]	ASTM D97	-5.3±0.2	-4.6±0.1	ASTM D97	-15 to 10	
Cold filter plugging point °C	-5 [347]	EN 116	-3.6±0.06	-3.2±0.05	EN 116	-	According to climate zone
Freezing point °C		ASTM D2386	-9.8±0.3	-8.3±0.7			
Flash point °C	152 [85], 132 to 140 [91], 152 [300]	ASTM D 7501	144.7±0.8	146.3±0.4	ASTM D 98	≥ 93	≥ 101

It is worth mentioning that all tests for the characteristics of the biodiesel were the average of three or more repetitions. The average values were recorded with the standard deviations.

The characteristics investigated were: Density, Specific gravity, API, Kinematic viscosity, Acid value, Iodine value, Cetane number, Carbon residue, Cold filter plugging point, Pour point, Cloud point, Freezing point, Flash point and Calorific value.

4.10.1 Evaluation of Camelina Methyl Esters Density, Specific Gravity and API

The fuel density is a mass measurement per volume unit and has a direct influence on the volumetric fuel consumption. The density, specific gravity and API values were determined and calculated for FAMEs which have been produced by TE process. The estimated values were (0.882 ± 0.7 g /ml at 15 °C), (0.887) and (28.02) respectively.

While, the determined values for the FAMEs have been produced from ISTE process under the same conditions were (0.886 ± 0.2 g /ml at 15 °C), (0.881) and (29.11), the results are illustrated in Table 4-20. Little differences between the current estimated values and those reported in the literature have been observed.

However, density, specific gravity, and API gravity are not included in specifications outlined in the ASTM standards for petrodiesel (D 975), biodiesel (D 6751), or biodiesel/petrodiesel blends (D 7467), a minimum API gravity at (30°) is recommended to maintain good power production and fuel economy for engine manufacturers [286]. Therefore, and according to API gravity values, Camelina FAMEs produced from ISTE process was nearest to the minimum value recommended.

The importance of density determination is owing to that density has direct effects on fuel performance, while cetane number, heating value and viscosity strongly correlated requirements of the engine. The density of the fuel also affects the quality of atomization and combustion. Moreover, the density is also important for defining the conditions of manufacturing, storage, transportation and distribution process of biodiesel. Lowering the fuel density causes the reduction of the particulates emission. In some cases, lower fuel density also causes the decrease of the nitrogen oxides emission. Besides, decreasing the fuel density is linked with the drop of its calorific value, which affects the engine performance. The density of esters depends on the molar mass, the free fatty acid content, and the moisture content [348] and [349].

While the specific gravity of biodiesel is dependable on the fatty acid composition of the mixed esters and their purity [350].

4.10.2 Evaluation of Camelina Methyl Esters Kinematic and Dynamic Viscosity

Viscosity is the most important property of biodiesels since it affects the operation of fuel injection equipment. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity by a factor of about eight [1].

Viscosity in general refers to a fluid's resistance to flow at a given temperature. Kinematic viscosity measures the ease with which a fluid will flow under force. It is different from dynamic (absolute) viscosity. Kinematic viscosity is obtained by dividing the dynamic viscosity by the density of the fluid. If two fluids with the same absolute viscosity are allowed to flow freely on a slope, the fluid with higher density will flow faster because it is heavier. The viscosity of a biodiesel is higher than the viscosity of fossil-diesel and some researchers have reported that the biodiesel viscosity can be up to (1.6) times that of diesel at (40 °C). This ratio increases especially when the temperature is below (25 °C) [351] and [352].

The highest acceptable kinematic viscosity for biodiesel as specified in D 6751 is (6.0 mm^2/s). While (EN 14214) the biodiesel standard for the European market, specifies a viscosity limit for biodiesel of 3.5–5.0 mm^2/s. If a batch of biodiesel does not meet this specification, the viscosity can be corrected by blending it with a fuel that has a lower or higher viscosity [181].

In addition, the higher viscosity of biodiesel fuel affects the start of injection, injection pressure and the fuel spray characteristics, which are the main parameters that affect engine performance and exhaust emission [352] and [353].

Influencing factors on viscosity are chain length, position, number and nature of double bonds, as well as nature of oxygenated moieties. In some cases, the viscosity of the fatty acids comprising a certain feedstock may affect the utility of the resulting esters as biodiesel fuel. Branched esters, which have improved low-temperature properties, are competitive with other esters in terms of kinematic viscosity and previously determined cetane number [353].

The kinematic viscosity values for Camelina FAMEs from TE and ISTE recorded in Table 4-20 were; (4.13 ± 0.01 and 3.58 ± 0.03 cSt) respectively, while the determined dynamic viscosity values were (3.64 and 3.17 cP) respectively. The results obtained in the current work revealed that the kinematic viscosity values are consistent with their values in other studies, also its meets the accepted limits set by ASTM D 6751-09 and UNE-EN 14214.

4.10.3 Evaluation of Camelina Methyl Esters Acid Value

Acid value or neutralization number is a measure of free fatty acids contained in a fresh fuel sample as well as of free fatty acids and acids from degradation in aged samples.

High fuel acidity is associated with corrosion and engine deposits, particularly in the fuel injectors which is why it is limited in the biodiesel specifications. High iodine value for biodiesel is due to the increased content of unsaturated fatty acid esters is susceptible to thermal as well as oxidative degradation processes. These degradation products lead to significant changes of the chemical composition of the fuel e.g. formation of polymerized products, acids, aldehydes, ketones, and others. Indicators of such products are measurable by changes of acid value, viscosity, ester content, linolenic acid ester content, stability, carbon residue, and contamination of the biodiesel. Therefore, a comparison of the different indicators will demonstrate that iodine value itself is not always the most suitable parameter to predict biodiesel behavior [182] and [354].

While, fuel that has oxidized after long-term storage will probably have a higher acid value, thus this parameter can also be used to measure the freshness of the biodiesel [348].

The reason of that the unsaturated molecules contribute to decreased the biodiesel oxidation stability, which is lower than diesel fuel, is that the unsaturated molecules promote to auto-oxidation, especially poly-unsaturated (e.g. linoleic acid), which are twice more reactive than mono-unsaturated, due to the oxidation process begin when an atom of hydrogen of a carbon adjacent or between two double bond is removed that have the lowest bond energy. In this process can be generated acids, aldehydes, aliphatic alcohols, ketones and insoluble sediments, which are mainly produced during autoxidation phase and that affect negatively biodiesel properties. These products increase peroxide value, viscosity, density, lubricity, iodine value, iodine value [355], [356] and [357].

The acid value of the Camelina FAMEs produced from TE and ISTE processes were (0.38 ± 0.04 and 0.33 ± 0.1 mg KOH/g) which is within the ASTM D 6751-09 and UNE-EN 14214 standards [358].

4.10.4 Evaluation of Camelina Methyl Esters Iodine Value

The iodine value (IV); or iodine adsorption value or iodine number or iodine index is the measure of unsaturation degree in oil. It is constant for particular oil or fat. Iodine value is a useful parameter in studying oxidative rancidity and chemical stability properties of different oils and biodiesel fuels. Higher quantity of double bonds in the sample has greater potential to polymerize and hence lesser stability [359].

The iodine value of the Camelina biodiesel produced by TE and ISTE process were (142 ± 0.7 and 145 ± 0.03 g I_2 /g) respectively, which is lower than all the other values mentioned in the literature as shown in Table 4-20.

Although the ASTM D6751 standard does not contain an IV specification, the EN 14214 standard limits the IV to a maximum value of (120 g I_2/ g). The high IV value may be correlated with the presence of considerable amount of unsaturated fatty acids in

Camelina oil. Engine manufacturers have long argued that biodiesel with a high iodine value tends to polymerize and form deposits on injector nozzles, piston rings and piston ring grooves when these surfaces are heated [360] and [85].

The tendency of polymerization increases with the degree of unsaturation of the fatty acids [348]. Also it is worth to mention that IV value often increases initially in the early stages of oxidative decomposition but will later decrease when the hydro-peroxides begin to decompose [361].

4.10.5 Evaluation of Camelina Methyl Esters Cetane Number

Cetane number (CN) is an important parameter for evaluating the quality of biodiesel. Conceptually similar to the octane number for gasoline, it is the prime indicator of biodiesel ignition performance inside combustion cylinder [362].

It relates to the ignition delay time of a fuel upon injection into the combustion chamber. The CN is a measure of ignition quality of diesel fuels, and a high CN implies short ignition delay. The higher the biodiesel cetane number, the quicker the ignition, in general the CN of biodiesel is generally higher than conventional diesel. The CN of biodiesel from animal fats is higher than those of vegetable oils [363], [364] and [1].

Fuels with low CNs tend to cause diesel knocking and have increased gaseous and particulate exhaust emissions due to incomplete combustion [365]and [85], and show increased gaseous and particulate exhaust emissions due to incomplete combustion. Moreover, excessive engine deposits are reported [183].

The cetane number value for the Camelina biodiesel produced by TE and ISTE processes were; 54.8 ± 0.5 and 53.6 ± 0.2 respectively as shown in Table 4-20. The limits for cetane number specified in the ASTM D6751 and EN 14214 standards are 47 and 51, respectively, thus, the CN values were highly satisfactory according to the EN 14214 and ASTM D6751 standards.

The cetane number depends on the chain length and the number of double bonds: it increases with increasing length of the fatty acid chain and decreases with an increasing number of double bonds [366].

In addition to the fact that the CN gives an idea of the fuel quality and the time required to start ignite, CN was also correlated with percentage of Camelina biodiesel in the blends according to the following equation, where β is the weight percentage of *Camelina sativa* biodiesel [85]:

$$\mathrm{CN} = -0.0813\beta + 50.886 \qquad \text{Eq. 4-9}$$

4.10.6 Evaluation of Camelina Methyl Esters Carbon Residue

Carbon residue gives a measure of the carbon depositing tendencies of a fuel oil. While not directly correlating with engine deposits, this property is considered an approximation [363].

Carbon residue is a test which measures the non-volatile compounds present in the fuel. The carbon reside of the methyl ester cannot be improved. It is a function of the characteristics of the feedstock. A way to manage this is to blend the fuel with biodiesel made from different feedstock which has a low carbon residue, such as virgin Canola, refined Soy, or tallow. Blending ratios would need to be experimentally determined [367].

The carbon residue results from Camelina FAMEs by TE and ISTE process were; (0.016 ± 0.3 and 0.052 ± 0.01) respectively, these values were satisfactory according to ASTM D 6751 standards which limited the value of carbon residue to be as a maximum 0.05 produced from burned all the sample (≤ 0.05 100% sample) and UNE-EN 14214 standards which limited the value of carbon residue to be as a maximum 0.3 produced from 10% from the samples remained after distillation process (≤ 0.3 on 10% distillation residue).

The carbon residue parameters considered as one of the most important biodiesel quality criteria, as it is linked with many other parameters, carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst or contaminants. Higher carbon residues may be due to the contaminant which might have entered the sample during the heating in the production of biodiesel and the presence of small amount of glycerol left in the final product [368] and [358].

4.10.7 Evaluation of Camelina Methyl Esters Cold Flow Properties

Cold flow properties of a fuel define its behavior in a given climate conditions. The cold flow properties are expressed in terms of Cloud point (CP), Pour point (PP), Cold filter and plugging point (CFPP). There are no European or US specifications for low temperature properties (each country is free to determine its own limits according to local weather conditions). The Cold Flow properties of biodiesel depend on the type of methyl-ester constituents and they are generally opposed, i.e., a biodiesel with good oxidative stability exhibits bad CFPP. It has also been documented that contaminants may originate from parent vegetable oils or be introduced during the transesterification, purification and even storage processes of biodiesel may affect cold flow properties. Bad cold flow properties may result in fuel line and pump blockage which creates problems for engine ignition, ultimately leading to fuel starvation. It is well known that biodiesel fuels have higher cold flow properties than mineral diesel fuel, due to high content of saturated fatty acids. In order to improve these properties, there are some options must be selected. These options which used to improve cold flow properties in the biodiesel can be finding mixture ́s oils with a high content of unsaturated fatty acids, oil fractionation, Alkyl esters structure modification and additive use. It was observed throughout researches that some of them can improve cold flow properties up to (20 °C) [369], [83] and [357].

Cloud point (CP) is defined as the temperature at which biodiesel starts forming cloudy suspensions and visible crystals. Generally, a relatively high CP value indicates a poor cold flowability. CP has been related to biodiesel composition in some published works [370] including degree of unsaturation such as CP decreases with increasing unsaturation degree. Although Camelina biodiesel inherently contains a high percentage of unsaturated fatty acid esters. The Cloud point value has been determined for Camelina FAMEs produced by TE and ISTE process , the estimated CP values were; (-1 ± 0.04 and 0 ± 0.02) respectively which are lower than other values for Camelina biodiesel reported in literature [54], [266] and [274]. The results reflect a positive mark.

Nevertheless, although the value of CP well represents biodiesel cold flow properties, it cannot alone, adequately assess biodiesel's low temperature operability or performance in vehicle tanks and fuel systems [83].

The cold flow properties of biodiesel are extremely critical in assessing the quality of biodiesel. The poor cold flow ability is a common concern in the biodiesel industry as all diesel fuels should be susceptible to start-up and be operational at low-temperature under cold weather conditions. This is mainly caused by the formation of crystals and solid precipitates at low temperatures, which could clog the vehicle fuel lines and filters [369].

Also, the Pour point PP values were determined for Camelina FAMEs which have been produced by TE and ISTE process. The estimated PP values were; (-5.3 ± 0.2 and -4.6 ± 0.1) respectively. The obtained PP values satisfy ASTM D 6751 standards which limited the value of PP to be as a (-15 to 10).

To reduce PP significantly one only needs to change the shape of the wax crystals while to improve operability the size and the shape of the wax crystals also need to be modified [371].

Finally, Cold filter plugging point CFPP, was determined for Camelina FAMEs produced by TE and ISTE processes. The estimated CFPP values were; (-3.6 ± 0.06 and -3.2±0.05) respectively. It is well noticed that biodiesel as a general expression has higher CFPP than diesel oil [372].

4.10.8 Evaluation of Camelina Methyl Esters Freezing Point

Freezing point FP value has been also determined for Camelina biodiesel produced by TE and ISTE processes. The estimated FP values were; (-9.8 ± 0.3 and -8.3 ± 0.7) respectively.

Biodiesel has freeze point in the range (-6.6 to -1.1 °C) higher than that of petroleum diesel. If the fuel begins to freeze (gel), it can clog filters and eventually become so thick that it cannot be pumped from the fuel tank to the engine [373].

There are no European or US specifications for freezing points (each country is free to determine its own limits according to local weather conditions).

4.10.9 Evaluation of Camelina Methyl Esters Flash Point

Flash point value is used to classify fuels for handling, transport, storage and distribution according to hazard level. In addition, this parameter may be used to detect contamination of fuel samples. The reason why the flash point value specified by the quality standards is relatively high are; to make the storage and transport purposes more safety and also to ensure that the alcohol is removed from the finished product. Low flash points may indicate alcohol residue in biodiesel [358].

The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. Flash point varies inversely with the fuel's volatility. For biodiesel, the minimum flash point is 93 °C in the United States, 100 °C in Brazil and 120 °C in Europe. Biodiesel's flash point decreases rapidly as the amount of residual (un-reacted) alcohol increases (methanol's flash point is 11–12 °C). Thus, measuring the biodiesel flash point helps to indicate the presence of methanol or any others alcohols have been used in biodiesel productions [348] and [374].

Flash point value has determined for Camelina biodiesel produced by TE and ISTE processes. The estimated Flash point values were; (144.7 ± 0.8 and 146.3 ± 0.4) respectively, these value were much higher than of (93°C and 101°C) as defined in ASTM D 6751 and UNE-EN 14214 standards respectively, implying that Camelina biodiesel is safer to be handled during the process of transport and storage [67].

In summary, most of the physical properties values of the biodiesel manufactured in the current study seemed to adhere to the specifications in ASTM D6751 and EN 14214 standards with just one exception for the iodine value which was not consistent with EN 14214 standards. This may be due to the existence of considerable amount of double bonds in the composition of Camelina oil and then Camelina methyl esters.

Nevertheless, the results estimated in the recent work were in most cases consistent with the results reported in literature. However, higher cetane number and cold filter plugging point and lower iodine number were recorded compared to those reported elsewhere.

4.10.10 Evaluation of Boiling Range for Camelina FAMEs

The boiling point of organic compounds can give important information about their physical properties and structural characteristics. Boiling point helps identify and characterize a compound. A liquid boils when its vapor pressure is equal to the atmospheric pressure [375].

The temperature of biodiesel evaporation depends upon the length of the fatty acid ester carbon chains; high contents of mono and poly unsaturated compounds. The characteristic biodiesel distillation curves have several impacts on engine operability and emissions. The high boiling range of fatty acid methyl esters has been linked with a gradual dilution of the lubricating oil by unburned fuel, which can result in serious engine damage Moreover, the high boiling range of biodiesel is also associated with the presence of unburned fuel in biodiesel exhaust gases at low engine temperatures, suggesting that under conditions of engine idling, the concentration of thermally decomposed, short-chain ester compounds is low, whereas intact esters may partly condense and thus escape combustion [376], [377] and [85].

ASTM–D 1160 distillation experiments were carried out on a sample of Camelina biodiesel prepared by ISTE in this study (DIC-textured *Camelina s*. seeds, at steam temperature T: 157.7 °C, and treatment time: 40.6 s; Exp. No. 5), and a sample from locally petroleum-derived diesel fuel (Kirkuk diesel).

The data estimated from the distillation experiments are shown in Table 4-21. The data were analyzed and the corresponding distillation curves were plotted as shown in Figure 4-18. This showed that the distillation curve of the biodiesel from Camelina proceeded with much higher initial boiling temperature (291 °C) and little higher final boiling temperature (361°C), moreover, it exhibited gentler slope and narrow boiling range (261-361), compared to that for petroleum diesel (initial boiling point =150 °C, Final boiling point = 360 °C, and boiling range (150-345 °C).

Table 4-21. Boiling range for Camelina FAMEs and Kirkuk diesel

Biodiesel (ml)	B.P for Camelina biodiesel (°C)	B.P for Kirkuk diesel (°C)
0 (Initial boiling point)	291	150
10	297	185
20	321	202
30	329	222
40	334	236
50	341	253
60	348	269
70	352	288
80	358	311
90 (Distillation temperature AET, 90%)	361	345
100 (Final boiling point)	366	360

The reason beyond this phenomena may be attributed to the higher boiling temperatures of the initial volatile (the boiling point of each of the methyl esters C18:0 is 351.58, C18:1 is 348.85, C18:2 is 365.85 °C), and to the less number of the FAMEs components of biodiesel [378] and [379].

However, according to the ASTM-D 6751 standard, the average final boiling point correspond to 90% recovered is 360 °C which is very close to that obtained for Camelina biodiesel distillate (361 °C). The results obtained gave a confirmation that the biodiesel prepare in this study meets the ASTM-D 6751 standard limit.

The distillation temperature of Camelina biodiesel has received very little attention in the literature, accordingly, the distillation test specification is not included in the European standard (EN 14214) [85].

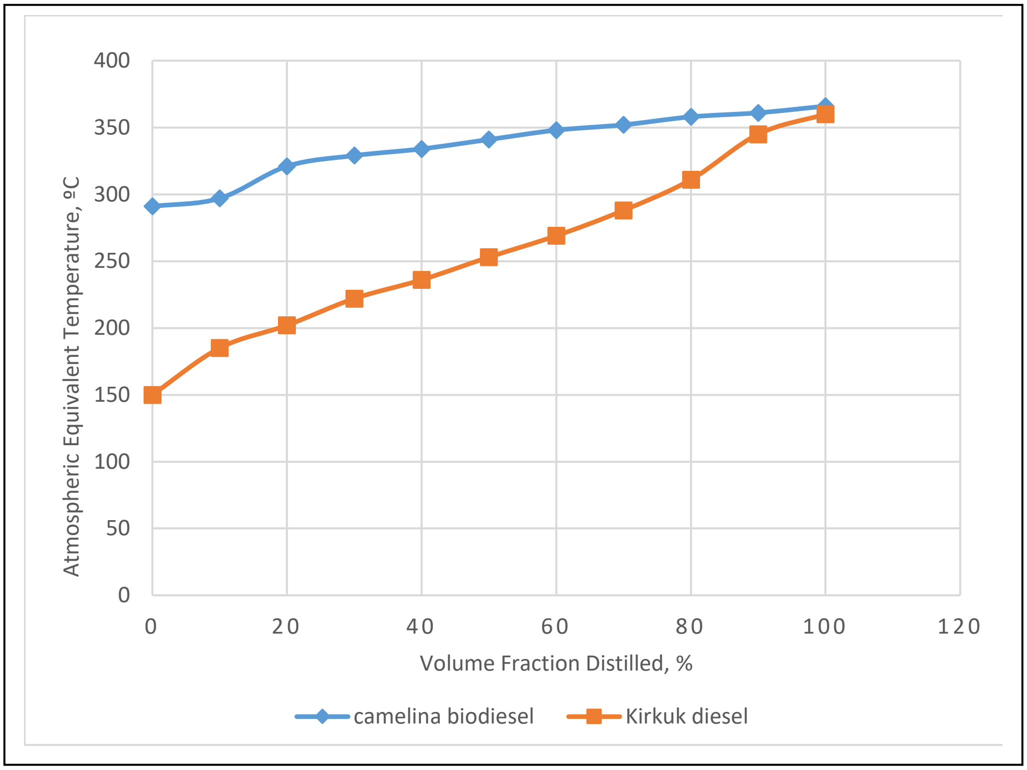


Figure 4-18. Distillation curves of Kirkuk diesel and Camelina biodiesel

CHAPTER 5. INDUSTRIALIZATION

5.1 Background

Although *Camelina sativa* as oleaginous seeds has obvious advantages as a feed of wonder health benefits, it has been recommended as a highly promising environmental sustainable energy crop in an ideal production platform for biofuels and industrial feedstocks.

The previous chapters described the studies carried out at laboratory scale to identify and quantify the impact of DIC parameters on yields of oil, and yields of oil esters obtained by conventional transesterification or by *in-situ* transesterification, all issued from Camelina seeds. In all these operations, texturing by Instant Controlled Pressure-Drop DIC is an exceptionally effective way to increase yields, DIC operating conditions were optimized relevantly to maximum yields.

DIC processing parameters were heating treatment time t (between 15 and 45 s) and the saturated steam temperature T (between 115.0 and 165.0 °C) which corresponds to pressure P (between 0.17 and 0.7 MPa). The optimized processing parameters (157°C or 0.58 MPa, and 40.6 s) were applied to identify the industrial significance of DIC process. Treatment capacity of the industrial scale DIC unit we studied in the present work was established to be about 8 tons/hour,

Figure 5-1.

The current chapter deals with the industrial significance of intensifying oil and biodiesel yields from Camelina seeds by inserting a pretreatment texturing stage of Camelina seeds using Instant Controlled Pressure-Drop (DIC) process, Figure 5-2, Figure 5-4, Figure 5-5, and Figure 5-6 show the industrial scale Instant controlled pressure drop (DIC) device, while Figure 5-2 is a lab-scale DIC unit.

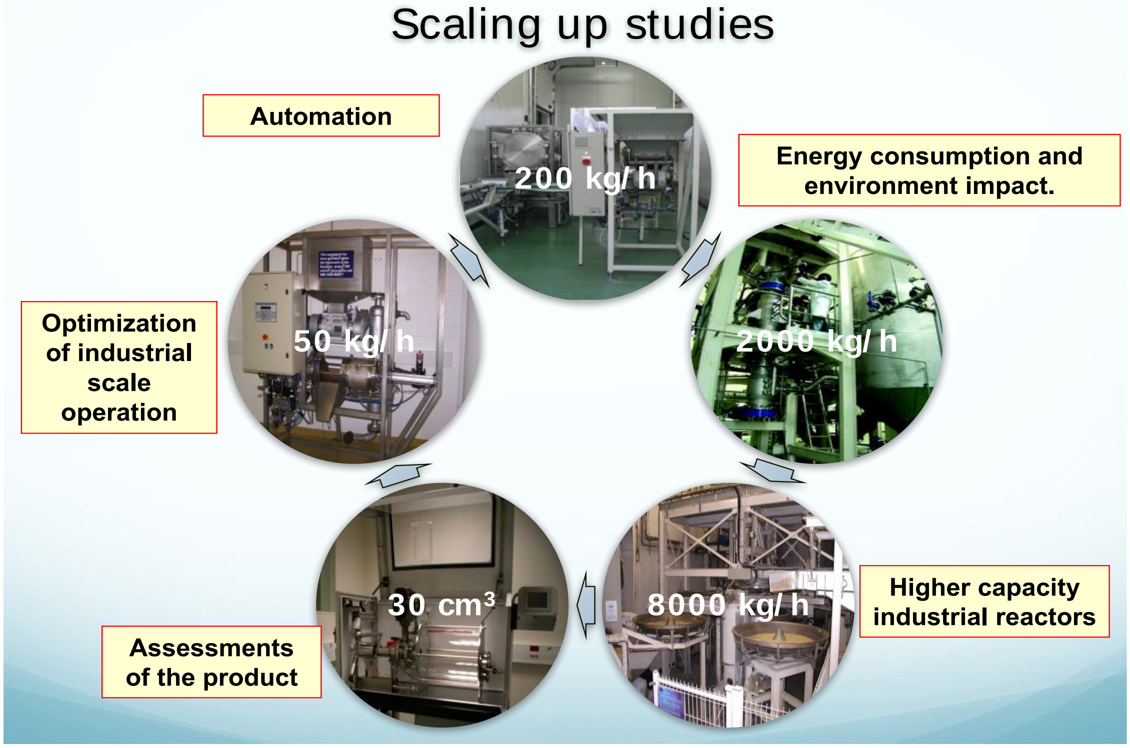


Figure 5-1. Strategy usually adopted for numerous industrial applications of Instant controlled pressure drop (DIC) technologies.

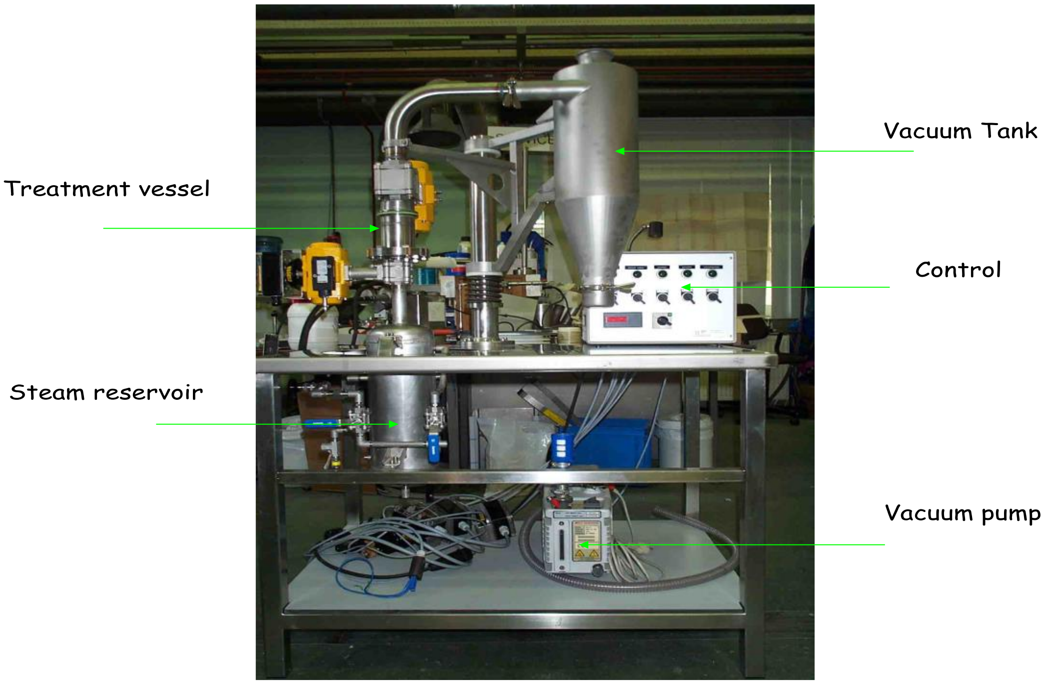


Figure 5-2. Lab-scale Instant controlled pressure drop (DIC) unit.

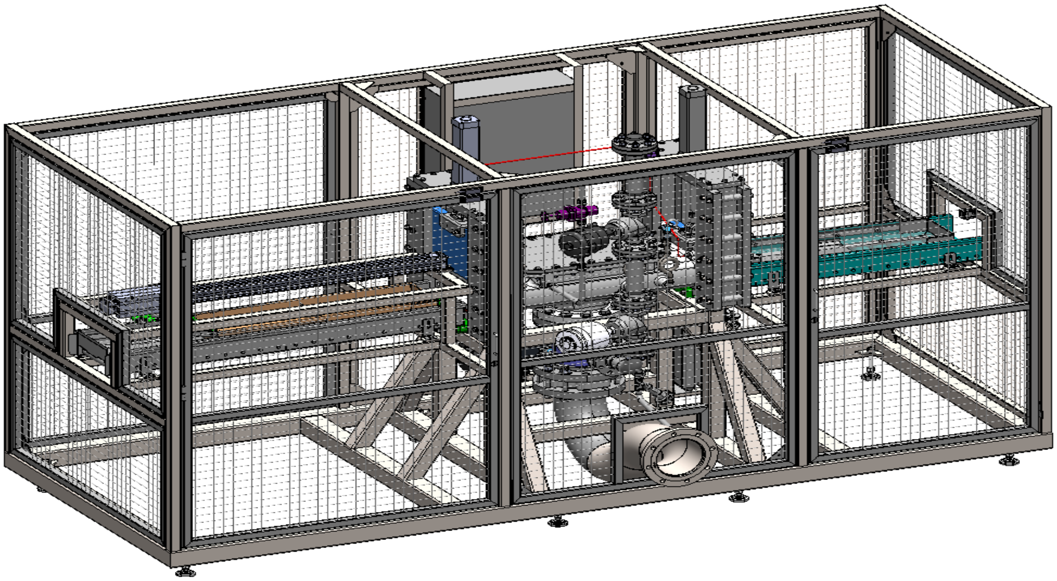


Figure 5-3. Instant controlled pressure drop (DIC) industrial unit

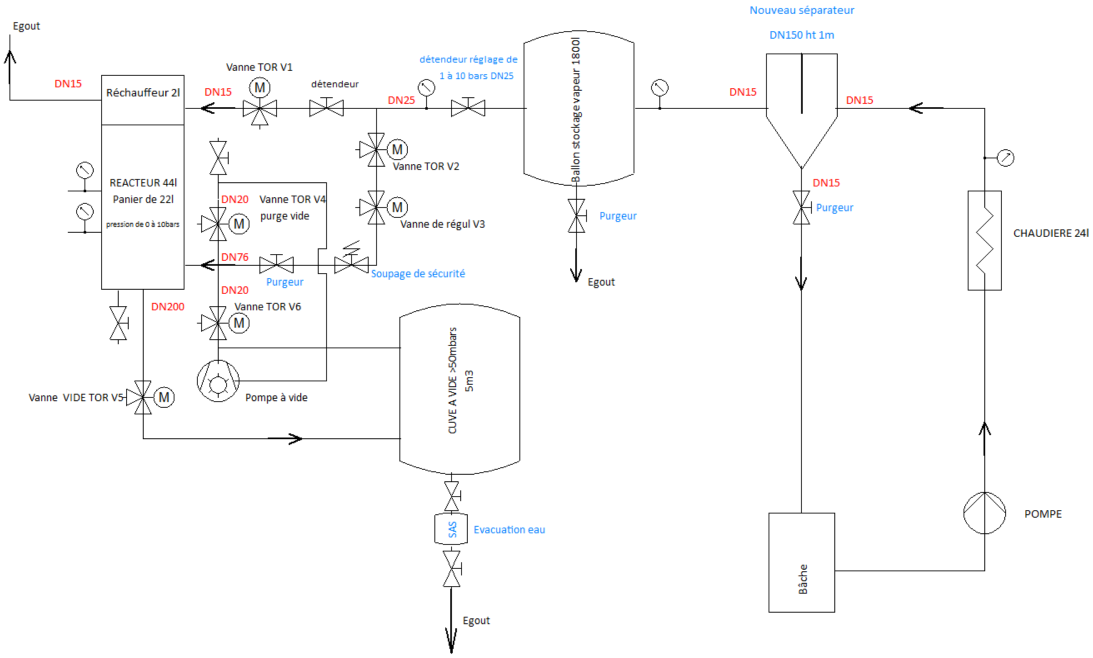


Figure 5-4. Instant controlled pressure drop (DIC) set-up

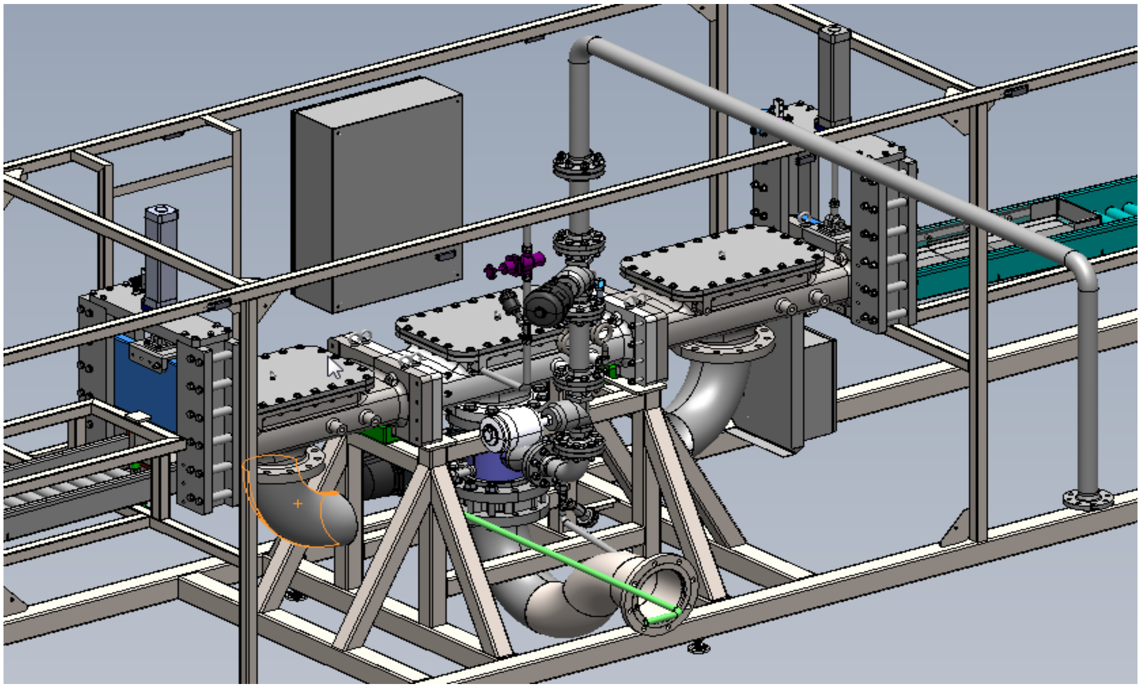


Figure 5-5. Multi-vessel Instant controlled pressure drop (DIC) industrial unit.

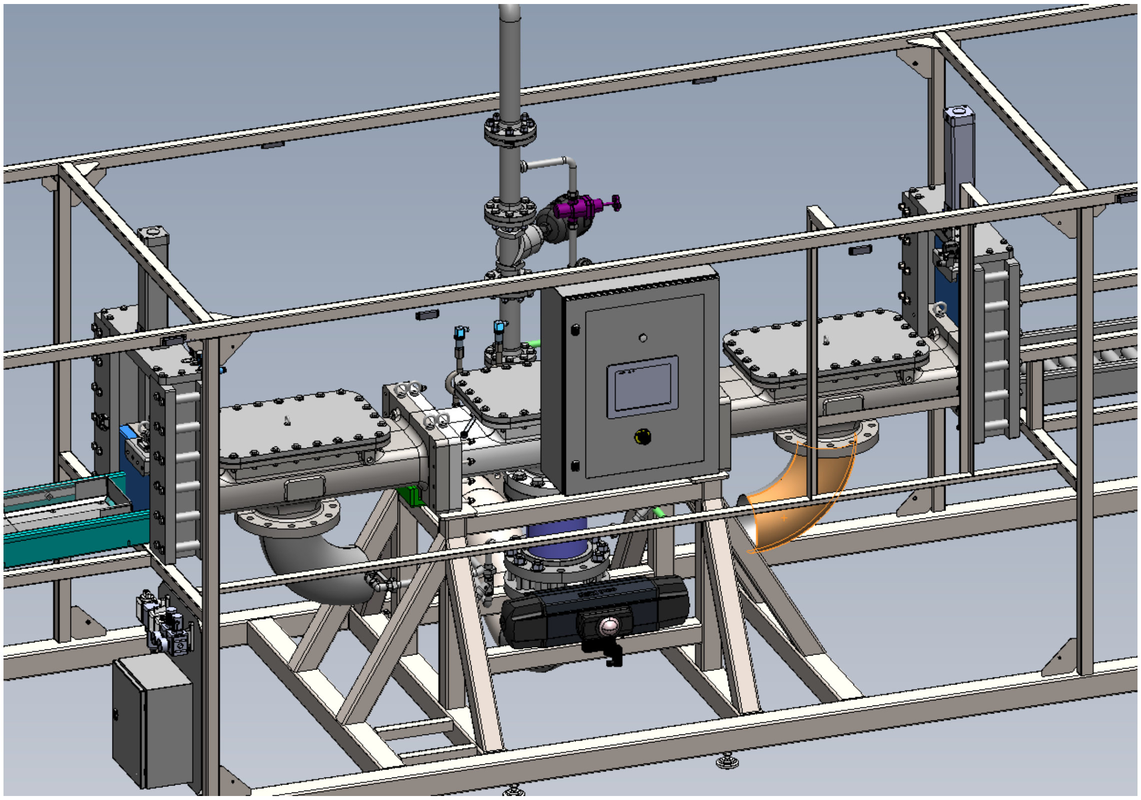


Figure 5-6. Industrial-scale Multi-vessel Instant controlled pressure drop (DIC) unit.

5.2 Comparative Industrial Yield of Oil

By using a mass input of 1000 kg Camelina seeds, it was possible to perform a comparative study of various extraction operations: a. Conventional transesterification of oil extracted by pressing (PO-TE), b. Conventional transesterification of oil extracted by solvent (SE-TE), c. Transesterification of pressed oil from DIC textured seeds (DIC/PO-TE), d. Transesterification of oil extracted by solvent (DIC/SE-TE), e. *In-situ* transesterification (ISTE) of un-textured raw material, and f. *In-situ* transesterification (ISTE) of DIC-textured seeds. Transesterification was carried out on oil produced from pressing and that from SE (solvent extraction) of Camelina cake.

By applying the optimized DIC texturing pre-treatment performed at 0.58 MPa for 40.6 s, the oil yield from both solvent extraction and pressing increased by an amount of 75.9 and 82.9 kg oil /1000 kg seeds, respectively. However, the pressing followed by SE of meal for DIC-treated seeds allowed a total increasing of the oil yield of 52.9 kg/1000 kg of seeds as shown in Table 5-1.

Table 5-1. Comparative Industrial amounts of extracted oil of various extraction operations from 1000 kg Camelina seeds and meals as raw material (RM)

	Amount of extracted oil RM (kg)	**Amount of extracted oil from DIC-textured seeds (kg)**	**Increased in yield after DIC textured (kg)**
Solvent extraction from seeds	352.5	428.4	+75.9
Seed pressing	218	300.9	+82.90
Solvent extraction from meals	85	55	-30.00
Total of pressing and SE of meals	303	355.9	+52.90

5.3 Comparative Industrial Yield of Biodiesel

The real values of DIC independent parameters and responses (biodiesel; FAMEs yield from TE and ISTE) carried out at laboratory are shown in Table 5-2.

Table 5-2. Real values of DIC independent parameters and responses (FAMEs yield from TE and ISTE)

Sample No.	Treatment temperature (°C)	Processing time (s)	ISTE-FAMEs (g/g db seeds)	TE-FAMEs yield (g/g db oil)	% ISTE-FAMEs (%g/g wb seeds)	% TE-FAMEs (% g/g wb oil)
Control	/	/	0.259	0.964	24.733	95.533
DIC (1, 4, 7, 10,13)	140	30	0.3790	0.975	36.01	96.465
DIC2	165	30	0.339	0.999	32.275	99.239
DIC3	140	45	0.326	0.974	31.045	96.388
DIC5	157.7	4.6	0.424	0.998	40.309	99.145
DIC6	157.7	19.4	0.353	0.947	33.650	93.770
DIC8	122.3	19.4	0.348	0.997	33.129	98.706
DIC9	122.3	40.6	0.339	0.994	32.226	98.384
DIC11	115	30	0.324	0.986	30.669	97.445
DIC12	140	15	0.315	0.947	29.968	93.719

The response analysis results of TE and ISTE processes are summarized in Table 5-3.

Table 5-3. Summary of Response Surface Modeling (RSM results estimated from Analysis of variance (ANOVA)

Process	Mathematical Equation	R^2 %	Optimum Conditions
TE – DB	$yield=-1.85809+0.380213t+0.377014S-0.0907241C-0.0291578t^2-0.0225087tS+0.0190261tC-0.00971189S^2-0.0133381SC+0.0192023C^2$	94.56	t,Time= 0.610628 (h) S, Solvent/oil= 17/1 (v/v) C, Catalyst/ solvent = 2%
ISTE- DB	$yield=12.3644+0.169793S+0.163447C+0.000663582S^2+0.000941933SC+0.00714877C^2$	97.57	S, solvent/seeds =50/1 (v/w) C, Catalyst/solvent =10%

A comparative study of an industrial production of biodiesel using 1000 kg of Camelina seeds was performed in the current work. Conventional Transesterification TE of Camelina oil, and *in-situ* Transesterification ISTE of un-textured raw seeds and the DIC-textured seeds resulted in great difference in biodiesel yield as shown in Table 5-4.

The optimized DIC parameters correspond to the optimum experimental results when applied to industrial scale resulted in a clear view for the industrial significance of the DIC process.

Table 5-4 shows the estimated industrial yield of biodiesel produced by TE and ISTE operations of 1000 kg of un-textured and DIC-textured Camelina seeds.

Table 5-4. Comparative Industrial yield of TE and ISTE operations in 1000 kg of un-textured and DIC-textured Camelina *seeds*

	FAMEs from RMs (kg)	FAMEs from DIC- textured seeds (kg)	Increased in yield after DIC textured (kg)
ISTE	247.3	403.1	155.80
TE	336.64	423.22	86.58

By incorporation of the optimized DIC texturing pre-treatment conditions, yield of biodiesel from both TE and ISTE increased as shown in Table 5-4. An increase in biodiesel yield of about 86.56 and 155.80 kg/ 1000g is produced from TE and ISTE respectively. Our findings are not in line with that recorded by other researches who reported that less amount of biodiesel is produced by ISTE compared to that produced by TE [243]. The result of the current work confirmed that when ISTE process is coupled with DIC treatment (DIC/ISTE) more biodiesel will be produced. The structure expansion and texturing of the raw material by DIC enhance the solvent diffusivity and extractability as well as the kinetics of the transformation process [313], [143] and [380]. The findings are of potential importance from industrial point of view in term of cost effective biodiesel production.

CHAPTER 6. CONCLUSION AND FUTURE RECOMMENDATIONS

6.1 Conclusions

The reason behind conducting the current research work is to produce biodiesel; the fuel of low sulfur content and high performance compared to the diesel fuel produced from fossil petroleum in Kurdistan region. Crude oils produced from some fields like those in Zakho region in particular Tawki oil fields contain high level of sulfur compounds. Desulfurization of the oil products such as gasoline and diesel oils is an expensive process which resulted in high fuels production cost. Moreover, Kurdistan region is very rich in wild plants that are considered as renewable resources for biofuels including biodiesel.

The biodiesel produced from natural resources may contribute to provide fuels for blending with the petro diesel to modify its ignition properties and engine performance reserving the petroleum sources and protect the environment from the undesirable emissions.

In this study, biodiesel (Fatty Acid Methyl Esters: FAMEs) were manufactured from Camelina seeds using conventional transesterification TE and *in-situ* transesterification ISTE techniques, in addition to apply innovative techniques using an Assisted Instant Controlled Pressure Drop process (DIC). The manufacturing processes were optimized using Response Surface Methodology (RSM) to optimize the operating variables of the processes that affect the biodiesel yield, as well as developing the mathematical models that explain the experimental results.

The optimized operating variables of the DIC pretreatment for the seeds are; operating temperature and time. The reason behind using the DIC process is its suitability to pretreat successfully natural products as highly improved in previous studies. Indeed, DIC technique did not affect the quality of oils and fuels produced, also did not lead to any decomposition of ingredients, that what was improved in this study. Another feature for

DIC technique is, the ability of treatment of large quantities of seeds in a short time, moreover, DIC technology is very economical techniques in terms of time and energy.

Camelina was chosen to be the raw material of the manufacture of biodiesel because it is not considered a food crop and has no competing with other crops on agricultural lands. Camelina has various preferences over other conventional oil crops, it is as a high oil content crops, has short season crop, in addition to its capability of withstanding drought and can tolerate low-quality, nutrient-poor soils, also it can be developed on marginal land.

Generation of Camelina biodiesel was proved that it is better than other crops used in biodiesel production like Canola and Jatropha in terms of estimated greenhouse emissions and net energy ratio. It provides more carbon to the soil, as well as it does not cause any damage to the soil. In addition to that, the cultivation of Camelina do not cause any damage to the soil due to its ability to provide more carbon to the soil, and then the soil converted it to the carbon dioxide, on contradiction with other crops like Jatropha which cause soil poisoning.

The first methods employed to produce biodiesel from Camelina triglycerides is transesterification TE process (the conventional process). This process involves reacting the raw material, with alcohol (methanol), solvent (toluene) and catalyst (sulfuric acid), TE process usually associated with extraction process to produced oil from the natural product by pressing and/or solvent extraction, the oil yield from these two processes was 0.2277 and 0.3681 g oil/g db seeds, respectively from the un-textured raw Camelina.

Increasing the oil percent from extraction process is very important issue from economical point of view, as well as using adequate experimental design to optimize the manufacturing process parameters on lab and bench scale to upgrade later the industrial production. Camelina seeds have been treated by DIC according to adopted experimental designs using RSM. The optimized processing conditions for DIC treatment that estimated from the model analysis were 157.7 ˚C as treatment temperature and 40.6s as a processing time.

It is worth to noting that oil yield increased up to (0.3153 and 0.4490 g oil/g db) by pressing and solvent extraction, respectively. The increase in amount of oil after DIC treatment of the seeds prior to pressing and solvent extraction processes accounted for 38% and 22%, respectively.

In order to prove the suitability of DIC treatment for producing biodiesel from Camelina seeds, chemical and physical properties of the oils and the biodiesel were determined and compared with those reported in literature. The results obtained in the current work approved that DIC treatment have no negative effect on oil and biodiesel quality, on the contrary, DIC treatment resulted in increasing the oil extractability and the yield of biodiesel, as well as DIC contributes to modifying some physical properties that may serve a lot in transforming Camelina oil for biodiesel production.

The biodiesel product by TE process, gave (0.9649 g FAMEs/g oil db), while DIC/TE process gave (0.9981 g FAMEs/g oil db), resulted in an increase of (3.44 %).

In-situ transesterification (ISTE) process; the single stage for producing biodiesel was applied on laboratory and industrial scale throughout the current study. The ISTE operating conditions were optimized by RSM in terms of solvent (Methanol: Toluene (90:10))/seeds ratio and catalyst H_2SO_4/Methanol concentration on biodiesel yield according to a 2-parameters experimental central composite design with (2^2=4) factorial points, (2*2) star-points and (5) repetitions of central point.

The results confirmed that the higher concentration of acid catalyst and solvent/seeds ratio, the higher the biodiesel yield. The optimized values of weight percent acid catalyst and solvent/seeds ratio were (10% v/v, catalyst: solvent) and (50:1 v/wt. solvent/seeds ratio), respectively for an optimized biodiesel yield of (0.4019 g FAMEs/g ddb) Camelina seeds. The adjusted regression coefficient value (R^2 = 95.80%) reflected the efficient capability of the model to explain the experimental results.

Biodiesel was also produced by ISTE from Camelina seeds pre-textured by DIC. The impact of DIC on the production process was also investigated using RSM. The innovative coupling of DIC texturing and ISTE have increased dramatically FAMEs yield up to (0.7731 g FAMEs/g ddb) compared to (0.3935 g FAMEs/g ddb) of un-textured raw Camelina seeds resulted in an increase of (96.46%). The results confirmed the high effectiveness of DIC in enhancing the biodiesel yield via ISTE.

Physical properties of DIC-ISTE and DIC-TE biodiesels produced in the current work were determined and compared with standards values and other values reported in literature. Most of DIC-ISTE and DIC-TE biodiesel properties values met the quality specifications in the EN 14214 and ASTM D6751 standards.

The boiling characteristics of biodiesel produced from Camelina seeds oil by DIC-TE were determined by vacuum distillation standard method, and compared those of petroleum diesel form Kirkuk fields. The initial and final boiling point of DIC-TE biodiesel was (291°C) and (366°C), respectively compared to (150°C) and (360°C) for the petrodiesel.

6.2 Recommendation

1. Working on local *Iraqi* Camelina is the first future perspective of this study. Our intensive investigations on local Camelina resulted in realizing that among ten Camelina genus types located in worldwide*,* just one type of Camelina (Camelina *rumelica)* is cultivated in our region, and therefore our future work will focus on working on Camelina *rumelica* for biofuels.

2. The other future recommendation is to write to the responsible in charge in Kurdistan region to planting of *Camelina sativa* with most crops, especially wheat in order to intensify the wheat cropping system, and increasing the soil fertility keeping in mind that it is very easy to separate these two seeds from each other depending on the difference between the two seeds size.

3. Another future recommendation is to modify the DIC-transesterification process by adding the solvent directly to the seeds in the treatment vessel during DIC treatment (Tripolium process) such as the extracted oil and the solvent could be withdrawn throughout special pipelines then recycled to the treatment vessel until achieving the optimum extraction. By this recycling process, time and energy will be saved, in addition to dispensing many of the glassware and apparatus.

4. The other future perspectives is to optimize (type of solvent, solvent to seeds ratio, temperature, time and agitation speeds). Also, to study the kinetics for the extraction and transesterification processes

5. A future perspective may be to investigate the DIC-TE and DIC-ISTE processes without using acid catalyst. Using alkali to speeding up the transformation reactions may be one of our future goals, in addition optimization the co-solvent by testing other co solvents including and not limited to tetrahydrofuran (THF), acetone, and petroleum ether.

6. Using RSM for modelling and optimization may be extended to optimize and model the processes based on the optimized conditions estimated from RSM of the current work, in order to identify more precise optimum operating variables for both TE and ISTE. Also, to develop some new mathematical correlations that express the relation between the studied parameters.

7. Full analysis of glycerol; the byproduct of the transesterification process will be one of our future perspectives, as well as carrying researches on its reusing in some innovative applications.

8. Finally, producing biodiesel from Camelina seeds by hydrocracking process is one of the future perspectives including studying the impact of DIC on the hydrocracking process.

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Résumé

La présente étude a eu pour objectif la comparaison de la fabrication du biodiesel à partir de graines de caméline suivant les procédés conventionnels ou assistés/intensifiés par Détente Instantanée Contrôlée DIC. La caméline est l'une des matières premières les plus adaptées à la fabrication de biodiesel puisqu'elle ne présente aucune concurrence aux cultures alimentaires et/ou à l'utilisation des terres agricoles. Son intérêt réside en sa teneur élevée en huile, sa courte saison de culture, ainsi que sa grande capacité à enrichir les sols pauvres, arides ou semi-arides.

L'insertion de la texturation par DIC permet l'intensification à la fois de 1/ l'extraction de l'huile suivie de transestérification et 2/ du processus de transestérification in-situ en une seule étape. Dans les deux cas, les analyses statistiques ont conduit, à l'aide de la méthode de surface de réponse (RSM), à des modèles mathématiques empiriques adéquats capables de mieux développer les résultats expérimentaux, d'optimiser les paramètres de traitement et de mieux définir le changement d'échelle. Le procédé DIC se distingue par son aptitude à réaliser avec succès l'expansion structurelle des produits naturels sans affecter la qualité des huiles et des carburants produits. L'augmentation de la quantité d'huile extraite après texturation des graines par DIC a été de 38% et 22%, respectivement pour le pressage et l'extraction par solvant. En mode ISTE, la texturation DIC a permis de doubler le rendement en FAMEs. En outre, la technologie DIC est une technique très économique en raison de la grande capacité de traitement due au faible temps d'opération et d'une consommation réduite d'énergie.

Abstract

The objective of this study was to compare the production of biodiesel from Camelina seeds using conventional methods or assisted/intensified by Instant Controlled Pressure-drop DIC. Camelina is one of the most suitable feedstocks for biodiesel production as it does not compete with food crops and/or agricultural land use. Its interest lies in its high oil content, short growing season, and great ability to enrich poor, arid or semi-arid soils.

The insertion of texturing by DIC allows the intensification of both 1/ extraction of the oil followed by transesterification and 2/ a single step in-situ transesterification process. In both cases, using the response surface method (RSM), statistical analyzes have led to adequate empirical mathematical models capable of better developing experimental results, optimizing treatment parameters and better define the scaling-up. The DIC process stands out for its ability to successfully achieve the structural expansion of natural products without affecting the quality of sensitive compounds such as oils and fuels produced. The increase in the amount of oil extracted after DIC texturing of seeds was 38% and 22% for pressing and solvent extraction, respectively. In ISTE mode, DIC texturing approximately doubled FAMEs yields (98% increased yields). In addition, DIC technology is a very economical technique due to its high processing capacity, low operating time, and weak energy consumption.