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GREEN DIESEL PRODUCTION

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E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "Green Diesel Production" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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YEŞİL DİZEL ÜRETİMİ

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Bu çalışmanın amacı, kanola yağının petrol hidrokarbonlarına dönüştürülmesidir. Çalışma iki grup altında yapılmıştır. Birinci grup çalışmalarda kanola yağı katalizörlü ve katalizörsüz ortamda farklı hidrojen basıncı, süre ve sıcaklıklarda "hidrotreating" işlemine tabi tutulmuştur. Katalizör olarak $NiMo/Al_2O_3$ ve Pd/C ticari hydrotreating katalizörleri kullanılmıştır. İkinci grup çalışmalarda, kanola yağının ağır vakum gaz yağı ile beraber işlenmesi incelenmiştir. Bu grup çalışmalar hidrokraking prosesi koşullarında gerçekleştirilmiştir. Katalizör olarak, DHC-8 ticari hidrokraking katalizörü kullanılmıştır. Her iki grup çalışmada da, reaksiyon koşullarının ürünlerin (sıvı ve gaz) verim ve özelliklerine etkisi incelenmiştir. Üretilen sıvı yakıtların yakıt karakteristikleri standart testler ile saptanmış, kimyasal yapıları ise spektroskopik (^{1}NMR, FT-IR) yöntemleri ile incelenmiştir.

Anahtar sözcükler: Kanola yağı, yeşil dizel, hidrokraking, hidrotreating

ABSTRACT

GREEN DIESEL PRODUCTION

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The aim of this study is to convert canola oil to petroleum hydrocarbons. The study was conducted under two groups. In the first group of studies, canola oil were subjected to "hydrotreating" process under different hydrogen pressure and temperature conditions with changing time intervals for both catalyzed and non-catalyzed environment. $NiMo/Al_2O_3$ and Pd/C commercial hydrotreating catalysts were used as catalysts. In the second group of studies, the processing of canola oil with heavy vacuum gas oil was investigated. This group of studies were carried out under hydrocracking process conditions. As the catalyst, DHC-8 commercial hydrocracking catalyst was used. The effects of reaction conditions, on the yield and properties of liquid and gas products were investigated on all studies. The fuel characteristics of the produced liquid fuels were analyzed by standard test methods while the chemical structures were examined by spectroscopic (^{1}NMR, FT-IR) methods.

Key words: Canola oil, green diesel, hydrocracking, hydrotreating

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SYMBOLS AND ABBREVIATIONS

Abbreviation	Explanation
° C	Celcius
$CDCl_3$	Chloroform-d
FCC	Fluid catalytic cracking
FID	Flame ionization detector
G	Gram
GC	Gas chromatography
HDO	Hydrodeoxygenation
^1H NMR	Proton nuclear magnetic resonance
HVGO	Heavy vacuum gas oil
Min	Minute
MPa	Megapascal
NMR	Nuclear magnetic resonance
T	Thermal
T.A.N	Total acid number
TCD	Thermal conductivity detector
WCO	Waste cooking oil

1. INTRODUCTION

Energy which is one of the basic need to continue the life is being used in every field. But the waste of energy sources causes also the environmental problems (Şenpınar and Gençoğlu, 2006). Increasing of the world population and development of industrial technology, the need of energy increases each day, and the continuity risk of it, causes big problems with the economies of developed or developing countries. Within the last 100 years, the consumption of energy has been increased 17 times more, also the necessity of energy is increasing approximately 4-5% each year. The approximate consumption of the world has been identified as 524 EJ per year. At 2020, it has been presumed that the consumption will increase 27% and at 2040 it will increase 65%. (British, 2013; EIA, 2013). Considering these rise, it is predicted that the fossil energy resources like petroleum, coal, natural gas, which has been used till today to provide the energy, will not be compensating the energy needs in the near future. For example, it is predicted that the reserves of resources of coal will be exhausted in 113, natural gas 55.1 and petroleum 53.3 years and will not be enough for the energy consumption. (BP Statistical Review of World Energy, 2014). There is an enormous need of a clean energy, considering that the fast consumption of fossil resources is giving an unrepairable damage to environment. (Karayılmazlar et al., 2011; Görez and Alkan, 2005).

The constitution of sera gas with consumption of fossil resources, especially the combination of greenhouse gas with the increase of carbon dioxide in atmosphere and changes on the velocity, blocks the heat exchange specification of atmosphere and causes global warming and subsequently the climate change. Because of the consumption of fossil resources the heat rate of world has reached the maximum levels of the last century, air pollution has incrassated, the quantities of storms and floods has increased dramatically. Also if the precautions will not be taken in near future the glaciers will be melted at 2020 and lots of countries will be flooded because of the water level increase. (Karakaya and Mercan, 2013; Uskan, 2009).

Instead of the fossil resources which right now effecting all population and next generation, the renewable and clean energy systems needs to be produced and preferred. Renewable energy can be identified as a type which causes less CO_2 emissions and less effect to environment, recycled constantly, and ready to be used at the nature with the hydraulic, wind, sun, geothermal, biogas, wave, flood energy, ebb and flood, hydrogen energy compared to fossil resources. (Irkıçatal Oğuz, 2014). On the other hand the biomass energy, which is obtained from biomass, if used as energy resource, is important for protecting the environment, as it can be used heat and electric production and also be used as liquid or gas fuel. (Topal and Topal Arslan, 2012).

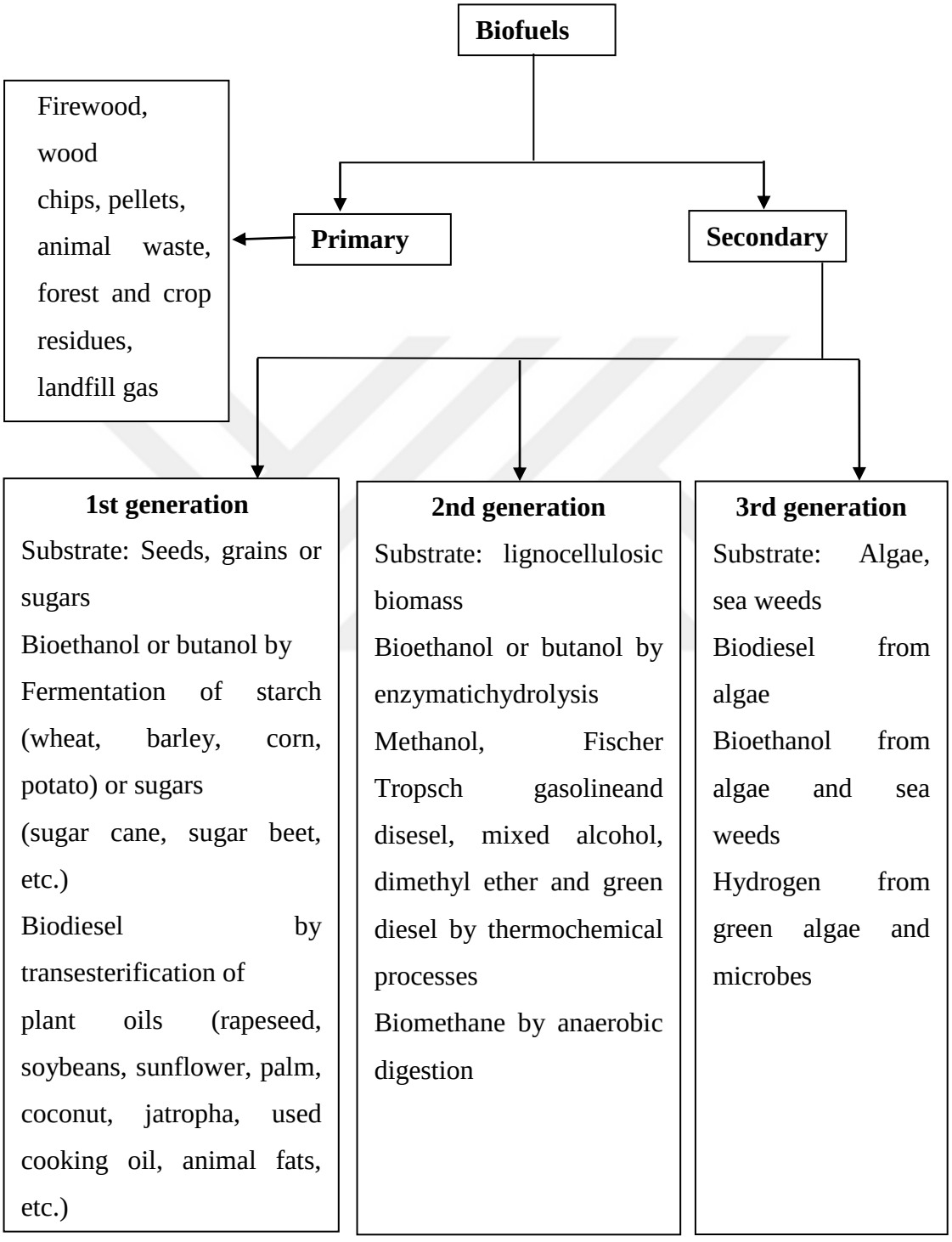
1.1 Biomass Energy

Biomass can be described as organic material resources, which has been produced with the storage of converted chemical energy from the photosynthesed solar energy from the green plants by using CO_2 and water. Biomass is the only recyclable, environmental friendly, creating less carbon emissions compared to fossil resources, and available for processing of energy and chemical raw material. (Wannapeera et al., 2011; Lee et al., 2013).

Biomass energy resources contain the all herbal and an animalic organic material, which main contents includes the carbohydrate. Biomass energy can be processed at the locations which culture plants, grass, fields, and energy plants grown, at the classical forest or artificial forests which been used for processing energy, at the water areas where the moss and algae grown, and also can be obtained from the biologically refined mugs which created by plants, animal wastes, household wastes and industrial wastes (Koçar, 2014).

Biomass energy can be classified as first-, second- and third generation biofuels.

Table 1.1 Classification of biofuels (Nigam, 2010)



1.1.1 First generation biofuels

Ethanol is first-generation biofuel which is produced by fermentation of sugar. Sugar can be extracted from cane, beets, or starch contained in corn kernels. Another alcohol derivates can be obtained by similar fermentation process.

1.1.2 Second generation biofuels

Second-generation biofuels are produced from lignocellulosic biomass. They are low cost and non-edible so using of them as fuels is so advantageous. They can be classified by types of the production process. It is shown in Figure 1.1.

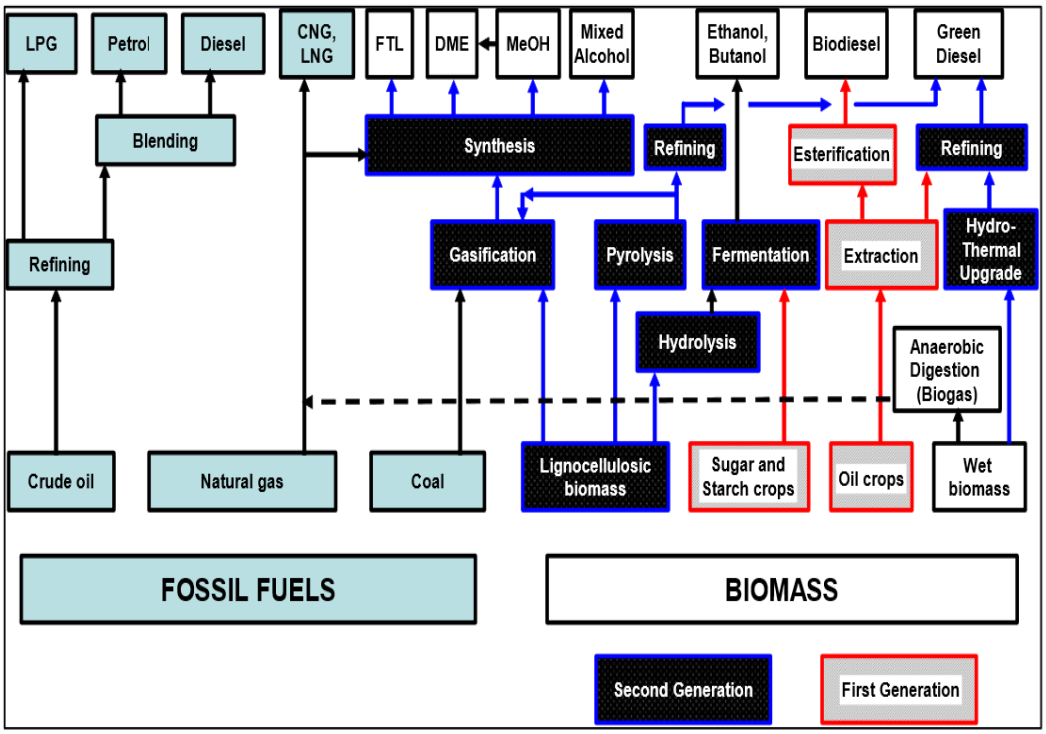


Figure 1.1 Biomass liquid fuel production process and comparison with fossil fuels process (Figure taken from United Nations Conference on Trade and Development, 2008)

1.1.3 Third generation biofuels

The third-generation biofuels are produced from macroalgae and microalgae. They are aforethought to be a practical alternative energy source. Because they have not disadvantages of first and second-generation biofuels. (Nigam, 2010). The algal biomass is more advantageous than planetary biomass. These advantages are; high growing rate (up to 20 g dry algae per m^2 per day), broad availability and non-edible. (Duman, 2014). Algal biomass can be used as raw material for co-firing to produce electricity, for liquid fuel production via thermochemical conversion (bio-oil), or for biomethane generation through fermentation. The hardness of this technology is producing third-generation biofuels while the high water and salt contents of macroalgaes. No need to transport nutrient and water for algae so we can save energy. (Wi, 2009)

1.1.4. Advantages of biomass as a source of energy

- Almost everywhere it can be growth
- Good experience in production and conversion technology
- Available for every range of production
- Available to operate in low light conditions
- Available for storing
- Needs a climate range between 5-35 °C
- Important in developing the social economic relations
- Not causing any greenhouse gas effect
- Not causing any acidic rain

2. RENEWABLE DIESEL (GREEN DIESEL)

Development of new energy sources instead of oil-based energy gains importance day by day. Much attention goes on producing fuel from biological sources or biomass. Renewable diesels have been growing popular among the various alternatives. Although produced from biomass it has same chemical structure of petroleum diesel. It is composed of long chain hydrocarbons. It is not an ester like biodiesel and has the same chemical properties with petroleum diesel. Mixtures at any proportion can be made with green diesel and petroleum diesel to be used as transportation fuel. Green diesel is another form of renewable diesel and the technology behind it is generally called as second-generation renewable diesel technology.

Renewable diesel should not be confused with biodiesel, because they have different production routes.

Biomass-to-Liquid (via Fischer-Tropsch)

Hydrotreated Vegetable Oil

Alcohol-to-Jet a) Synthesized Paraffinic Kerosene

b) Synthesized Kerosene with Aromates

Kerosene from Catalytic Hydrothermolysis („*ReadiJet*“)

The chemical composition of renewable diesel is the same with petroleum diesel. Comparing to biodiesel, renewable diesel has a number of advantage. The structure of renewable diesel doesn't have oxygen because of hydrogenation. Unlike biodiesel it will not cause freezing temperature and storage problems. Furthermore, thanks to its same chemical structure as petroleum diesel, engines that run on conventional diesel fuel can use green diesel without blending.

In addition, renewable diesel burns more effectively and cleanly than petroleum diesel.

2.1 Comparison of Renewable (Green) Diesel with Petroleum Diesel and Biodiesel

2.1.1 Petroleum diesel

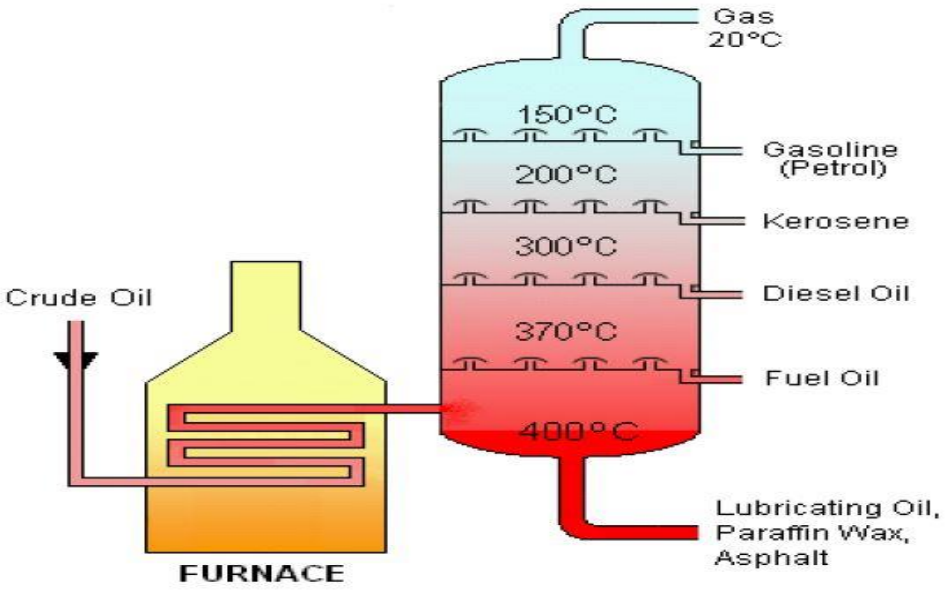


Figure 2.1 The fractional distillation of crude oil. (Yoon, 2011)

Before making a comparison between renewable diesel and biodiesel, it is wise to define petrodiesel clearly which everyone knows as diesel fuel.

Diesel fuel is produced by the distillation of petroleum. The crude oil distillation is carried out between 200 and 350 °C at atmospheric pressure. The petrodiesel is rich in paraffinic structures. It is a mixture of hydrocarbons containing 8-21 carbon atoms. The specifications of petrodiesel are defined by EN 590 in Europe and by ASTM D975-16a in USA.

2.1.2 Biodiesel

Producing of biodiesel is based on transesterification reaction between animal fats or vegetable oils with an aliphatic alcohol. Usually methanol and ethanol are used in this process. The by-product of the reaction is glycerol.

ASTM D6751-15c[e1] defines biodiesel as "a fuel comprised of alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats." Biodiesel can be also called, as rapeseed methyl ester (RME) or fatty acid methyl ester (FAME) because of its reactants names in Europe.

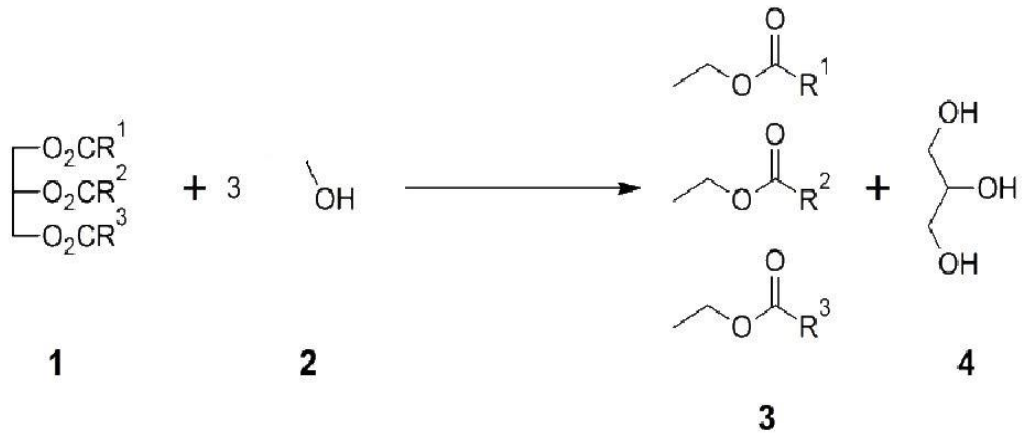


Figure 2.2 Biodiesel productions **(1),** Triglycerides from plant oil **(2),** Methanol **(3),** biodiesel **(4)** glycerol (Figure taken from http://www.government-fleet.com/).

Unlike petrodiesel and renewable diesel, biodiesel has oxygen atoms in its structure. This means, it has different chemical and physical properties.

Biodiesel can be mixed with diesel fuel or used as unmixed. 100 % biodiesel is referred to as B100. The blends can be named according to their biodiesel ratio. For example, a mixed fuel containing 40% biodiesel and 60% diesel fuel is called B40.

2.1.3 Renewable (Green) diesel

Renewable diesel is a type of fuel produced from biological sources. It is also called "second generation diesel" or "green diesel". The composition of renewable diesel does not contain esters and so it differs from biodiesel.

"Renewable diesel" covers all fuels like diesel, but it is produced from biological sources. The same nomenclature with biodiesel is used for naming renewable diesel blends. R100 means pure renewable diesel, where R40 means a

blend consisting of 40% renewable diesel and 60% petrodiesel. Renewable diesel can be mixed in any proportion with petrodiesel, but because of lubricity issues sometimes additives may be needed.

Table 2.1 The properties of petrodiesel, biodiesel and renewable diesel

Properties	Petrodiesel	Biodiesel	Renewable Diesel
Cetane	40-55	50-65	75-90
Energy Density, MJ/kg	43	38	44
Density, g/ml	0.83 - 0.85	0.88	0.78
Energy Content, BTU/gal	129K	118K	123 K
Sulfur, ppm	<10	<5	<10
NOx Emission	Baseline	+10	-10 to 0
Cloud Point, °C	-5	20	-10
Oxidative Stability	Baseline	Poor	Excellent
Cold Flow Properties	Baseline	Poor	Excellent
Lubricity	Baseline	Excellent	Similar

2.2. Hydrotreated Vegetable Oil

Hydrotreating process is used to produce hydrotreated vegetable oil. In petroleum refinery, hytrotreating process is used to remove the undesirable compounds such as condensed ring aromatics, nitrogen, sulfur or metals. The basis of this process is hydrogenation of vegetable oil under high temperature and pressure in the presence of a catalyst The obtained product is also named as "green diesel". The triglyceride molecules are turned into paraffinic hydrocarbons and impurities such as oxygen, sulfur and nitrogen are removed. During this process, propane is also produced as by-product.

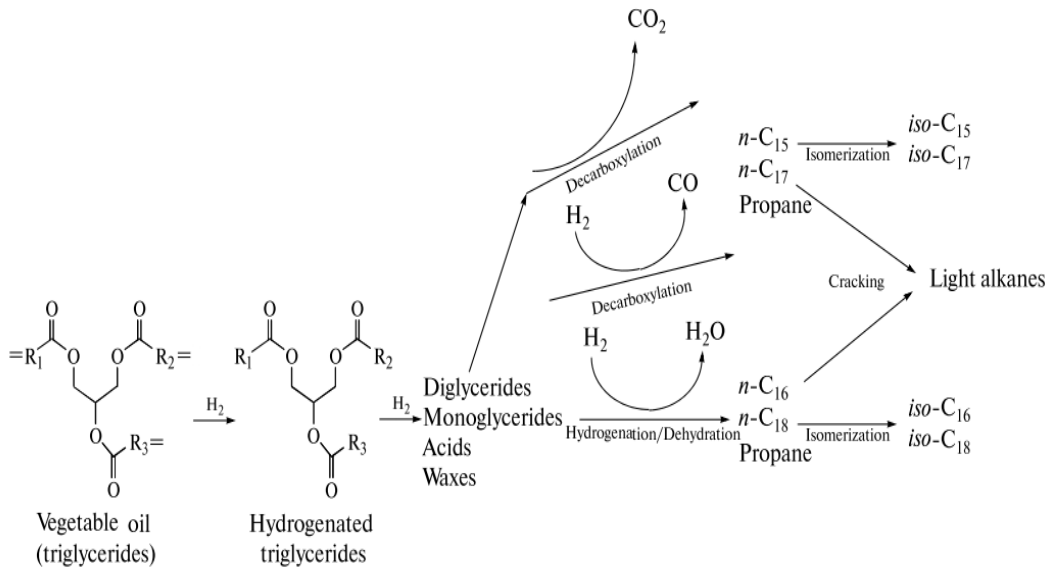


Figure 2.3 Scheme of the main reactions in the hydrotreatment of oil and Fatty Raw materials (Lavrenov, 2011)

Neste Oil is the largest manufacturer, producing 1,3 billion liters annually (Lehmus, 2014). The company has 4 plants (Finland, Singapore and Rotterdam) that are able to produce renewable diesel from a wide range of oils by hydrotreating process. On the other hand, many companies, such as Conoco Philips, Dynamic Fuels and Tyson Foods, are working together on a project for converting waste animal fat into renewable diesel.

As we mentioned above, all petroleum refineries use hydroprocessing, thus we can make renewable diesel blends at refineries. The advantages of using existing petroleum refineries when compared to constructing a green diesel refinery are still controversial.

Canola Oil

Canola oil is widespread oil produced from canola plants. Physical and chemical properties of canola oil is given in Table 2.2

Table 2.2 The physical and chemical properties of canola oil (http://www.cibaria-intl.com/themes/main/spec.php)

PARAMETER	SPECIFICATION
Organoleptic Characteristics:	
Appearance/Clarity	Clear, brilliant, yellow
Flavor/Odor	Bland
Color (Lovibond) Red	1.2 Max
Color (Lovibond) Yellow	1.2 Max
Typical Analysis Ranges:	
Free Fatty Acid (% m/m expressed in oleic acid)	0.05 Max
Moisture (%)	0.1 Max
Peroxide Value (mEq/kg)	1 Max
Iodine Value	108-126
Saponification Value	182-193
p-Anisidine Value	4 Max
Cold Test (>5.5 hours at 0 °C)	Clear
Refractive Index (40 °C)	1.465-1.467
Specific Gravity	0.912-0.914
Oil Stability Index (OSI) at 110 °C, (hours)	8 Min
Smoke Point (°C)	232 Min
Additives	None
Typical Fatty Acid Ranges:	
C 14:0 Myristic acid, (%)	0-0.2
C 16:0 Palmitic acid, (%)	3.3-6
C 16:1 Palmitoleic acid, (%)	0.1-0.6
C 18:0 Stearic acid, (%)	1-2.5
C 18:1 Oleic acid, (%)	52-70
C 18:2 Linoleic acid, (%)	16-25
C 18:3 Linolenic acid, (%)	5-14
C 20:0 Arachidic acid, (%)	0.2-0.8
C 20:1 Gadoleic acid (eicosenoic), (%)	0.1-4
C 22:0 Behenic acid, (%)	0-0.5
C 22:1 Erucic Acid, (%)	0-2
C 24:0 Lignoceric Acid, (%)	0-0.3

3. LITERATURE REVIEW

3.1 Hydrotreating of Vegetable Oil

Green diesel is an environmentally friendly liquid fuel produced by conversion of biomass. Hydrotreating process is used for the production of green diesel. In the course of hydrotreating, oxygen in triglycerides is removed by a catalyst at elevated temperature. There are three different routes of oxygen removal which are shown below:

(I) $R - CH_2 - COOH \longrightarrow R - CH_3 + CO_2$ (Decarboxylation)

(II) $R - CH_2 - COOH + H_2 \longrightarrow R - CH_3 + CO + H_2O$ (Decarbonylation)

(III) $R - CH_2 - COOH + 3H_2 \longrightarrow R - CH_2 - CH_3 + 2H_2O$ (Hydrodeoxygenation)

Kiatkittipong et al. (2013) investigated hydroprocessing of palm oil during its conversion to bio-hydrogenated diesel. Three different types of oil were studied. The researchers used simulated distillation (ASTM D2887-16a) for analyzing product distribution. For obtaining optimal reaction conditions, the effect of reaction parameters such as reaction time, internal temperature, initial pressure and catalyst types (Pd/C and sulfided $NiMo/\gamma\text{-}Al_2O_3$) were studied for each feedstock. The highest diesel yield of 51% were gained from hydroprocessing of CPO for 3 hours with Pd/C catalyst at 400 °C internal temperature and 4 MPa initial pressure. The highest yield obtained for DPO was 70%. The catalyst and the reaction conditions were the same with CPO except reaction time. The reaction of DPO was faster and completed in 1 hour. Higher maximum diesel yield (81%) was obtained from PFAD at lower temperature (375°C) in only 30 minutes. The best conversion performances for fatty acid feedstock were obtained with Pd/C catalyst whereas $NiMo/\gamma\text{-}Al_2O_3$ catalyst was found to give better yields for triglyceride feedstock. The diesel yield remained CPO < DPO < PFAD respectively. Reaction temperature, initial pressure and reaction time decreased in the order of CPO > DPO > PFAD.

Pinto et al. (2013) studied hydrotreating of canola oil during the production of bio-chemicals. The hydrogenation of canola oil was tested at fixed hydrogen

pressure (1.1 MPa) and variable reaction temperatures (200-400 °C) and reaction times (6-180 minutes). Mercantile Co-Mo catalyst was used to increase the reaction rate. The highest hydrocarbon yield (85%) without catalyst was achieved by the reaction of rapeseed oil with hydrogen for 120 minutes at 400 °C. The addition of catalyst to the reactor increased hydrocarbon yield to 92% at same conditions and reaction time. The hydrocarbon yield further increased to 97% when the reaction time was increased to 180 minutes with catalyst. Aromatic content of the products in above conditions were found to be 50%.

Šimáček et al. (2011) investigated producing of renewable diesel fuel by hydrotreating of sunflower oil. The hydrogenation of sunflower oil was tested at variable reaction temperatures (360-420 °C) and 18 MPa in a laboratory type fixed bed reactor using commercial hydrocracking catalysts. The yield of *n*-alkanes at product was found to be 67 %wt. at 360 °C reaction temperature. The increase of temperature to 420°C caused the *n*-alkane concentration to decrease to 20 % wt. Aromatic content of the final product increased more than 5 % wt by increasing temperature. It is evidence that compositions of the products directly affected by reaction temperature.

Veriansyah et al. (2011) investigated the effects of different types of catalysts on producing paraffinic hydrocarbon mixture from hydrotreated soybean oil. The conversion yields of the catalysts NiMo, Pd, CoMo, Ni, Pt and Ru at catalyst/oil weight ratio of 0.044 were 92.9%, 91.9%, 78.9%, 60.8%, 50.8%, and 39.7% respectively. If the catalyst/oil weight ratio was promoted to 0.088, conversion yield of soybean oil increased dramatically to 95.9 % with Ni catalyst. The catalyst/oil weight ratio did not have the same impact on other catalysts. The composition of the products was found to be significantly affected by the catalyst type. Ni, Ni-Mo, and Co-Mo catalysts were found to be preferable for their high conversion and relatively low cost for hydroprocessing of inartificial triglycerides.

Šimáček et al. (2010) examined hydrotreating of canola oil as a resource of hydrocarbon like biodiesel. Hydroprocessing of canola oil was achieved in a laboratory scale continous reactor. Commercial hydrotreating catalyst $NiMo/Al_2O_3$ was used to increase reaction rate. The experiments were done at

various temperatures (310 °C and 360 °C) and initial hydrogen pressures (7 and 15 MPa) Mixtures of 5 to 30% wt. of hydroprocessed rapeseed oil were prepared with petroleum diesel fuels and it was shown that hydroprocessed rapeseed oil increased cetane index by 2-14 units.

Kim et al. (2013) investigated effects of various reaction parameters with Ni and $CoMoS_x$ catalysts on the hydrotreating of soybean oil. The hydrogenation of soybean oil was done at variable reaction temperatures (300-400 °C) and variable initial hydrogen pressures (2.5-15 MPa) in batch and continuous reactors. The hydrotreating conversion, oxygen removal performance and diesel selectivity of Ni and $CoMoS_x$ catalysts were examined. The product composition was analyzed by gas chromatography. The results showed that oxygen removal performance of the catalysts and n-paraffin efficiency increased by increasing temperature in both reactors. Improving initial hydrogen pressure had positive affect on yield in batch reactors, on the other hand it had a negative effect in continuous reactors.

In a study conducted by Galadima and Muraza (2015), converting of vegetable oil to jet fuels like hydrocarbons by catalytic reaction with catalysts. They investigated the role of the heterogeneous catalysts for the transition of vegetable oils into paraffinic hydrocarbons like for jet fuels. They found that catalysts as Ni and Mo supported oxides are regarded so efficient for hydrotreatement operating though Pd and Pt supported on zeolites essential hydroisomerization catalysts. It is concluded that carbon numbers of jet fuels depends on the oil feedstock.

Jeczmionek et al. (2014) examined hydrotreating reactions like, hydrodeoxygenation, decarboxylation and decarbonylation during co-processing of vegetable oils with NiMo catalyst. They investigated affects of temperature at this study. In their study, two paraffinic feedstocks containing 20 vol. % of considerable various vegetable oils (olive or corn oil) were exposed to hydroconversion over a commercial hydrotreating catalyst (NiMo) under two different pressures (3.0 or 6.0 MPa), at 320 °C reaction temperature, with LHSV of 1.0 h^{-1} and hydrogen/feedstock rate equivalent to 300 N m^3/m^3. They found that the temperature effects changed noticeably when dissimilar vegetable oils

were used as feedstocks. It was found that the differences in the total temperature effects noted pending hydroconversion for the two vegetable oils depend on the unsaturated fatty acid contents. For the feedstock consisting of liquid paraffin with 20 vol.% olive oil, liquid product yield equaled approximately 71% for 3.0 MPa and 32% for 6.0 MPa. For the feedstock with the equal quantity of corn oil, these liquid yield were 67% and 29%, respectively. The results show that higher unsaturated fatty acid ingredients in the vegetable oil markedly improve the total hydroconversion heat impact.

Susanto et al. (2014) studied hydrodeoxygenation process with Pd/zeolite catalyst to produce renewable diesel. In their study, hydrodeoxygenation of oleic acid as sample compound of vegetable oils over Pd/zeolite catalysts was examined under conditions of 375-400 °C and 1.5 MPa in a laboratory scale stirred autoclave reactor. Pd/zeolite-1 and Pd/zeolite-2 catalysts were prepared using microwave polyol procedure with different process conditions. They found that the liquid hydrocarbon products called Renewable Diesel have convenient density and viscosity, and fairly high cetane index in accordance with standard commercial diesel and ASTM D975-16a. They also found that the IR spectrum of Renewable Diesel products have similarities with mercantile diesel. As a result the oxygenation removal pathway of oleic acid over particularly Pd/zeolite-1 catalyst was firstly compiled through decarboxylation.

3.2 Co-processing of Vegetable Oil with Petroleum Products

Huber et al. (2007) studied hydrotreatment of vegetable oils in heavy vacuum oil blends to produce premium diesel. The hydrotreatment of vegetable oils and blends of vegetable oil and heavy vacuum oil (HVO) was performed at 300-450 °C temperatures with commercial sulfided $NiMo/Al_2O_3$catalysts. They used sunflower oil and mixed 5 wt% sunflower oil - 95 wt% HVO feedstock for highest theoretic paraffinic liquid product yield. The research showed that hydrotreating vegetable oils for biofuel production is a good development for the future.

In a study Šimáček and Kubička (2010) investigated producing of diesel fuel from petroleum heavy fractions containing canola oil by hydrocracking process. In their study, hydrocracking blends of petroleum vacuum distillate and petroleum vacuum distillate including 5 wt.% of canola oil were performed at 400 - 420 °C and underneath 18 MPa hydrogen pressure with mercantile Ni–Mo catalyst. At the end of the reaction, kerosene, gas oil and the residual products were obtained by distillation. Diesel fuels, which were produced in co-processing at 420 °C, have low cloud and cold filter plugging point (cloud point: -23 °C, CFPP: -24 °C). These properties are very similar to traditional petroleum diesel properties. The research shows that producing of green diesel at refineries is possible by hydrocracking of petroleum heavy fraction and vegetable oil blends.

4. MATERIALS AND METHODS

4.1 Material

Canalo oil was commercially provided. The Heavy Vacuum Gas Oil (HVGO), which has a boiling point range 291-578 °C (Table 4.1), is feedstock of hydrocracking unit in Aliaga refinery, Izmir. The DHC-8 is a commercial catalyst used in the İzmir refinery. It is a shapeless bifunctional catalyst. It has both hydrotreater and hydrocracker functions. The commercial Pd/C and $NiMo/Al_2O_3$ catalysts are hydrogenation and hydrotreating catalysts, respectively.

Table 4.1 Properties of heavy vacuum gas-oil (HVGO)

Density, 15 C (g/cm^3)			0.9106			
Carbon Conradson (wt%)			0.36			
Sulphur (wt%)			1.83			
Distillation curve according to ASTM D7169-16						
% V	IBP	10	30	50	70	90
°C	290.9	358.9	408.1	442.0	477.3	521.6

4.2 Methods

4.2.1 Hydroprocessing experiments

Hydroprocessing experiments were carried out in a shaking-type autoclave (100 cm^3). In a typical run, catalyst and canola oil were mixed and put into the reactor. The reactor was stamped and flushed and pressurized by hydrogen. The temperature of reactor was increased at a rate of 5 K min^{-1} and was kept at this temperature during the reaction.

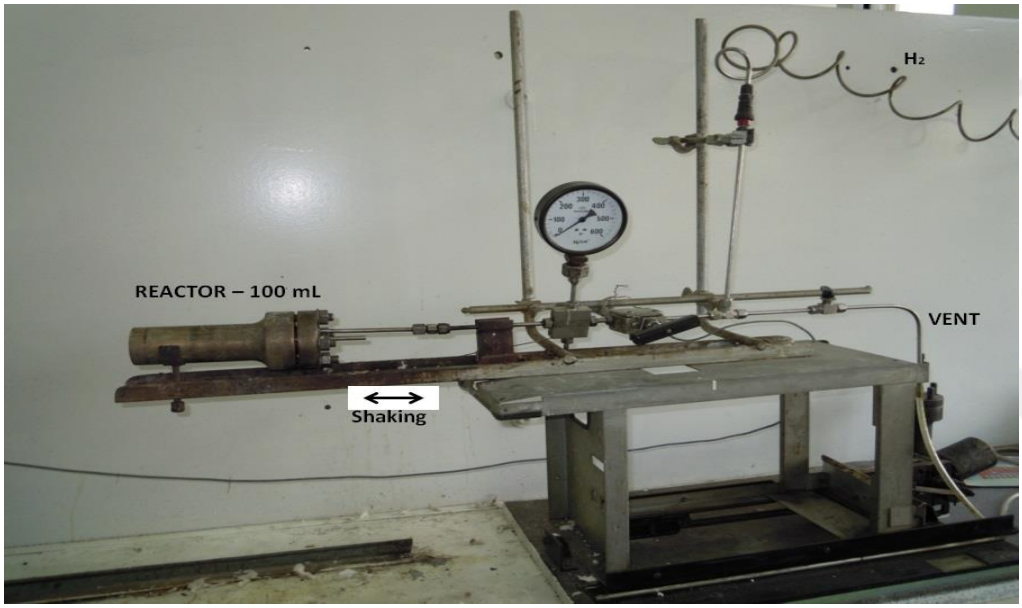


Figure 4.1 Experimental set-up

After reaction was completed, the temperature of reactor was reduced. Then using Tedlar bag the gaseous products were gathered. Solid and liquid materials were obtained individually by filtering. The hydroprocessing experiments were done at 350-450 °C temperatures, these experiments were taken of 0-120 min. with initial hydrogen pressures of 3 and 6 MPa.

In co-processing experiments, the mixture containing 80 wt. % of HVGO and 20 wt. % of canola oil was used as a feed. The catalyst and feedstock ratio was 1/10 in all experiments.

4.2.2. Analysis

4.2.2.1 Density analysis

The density of fraction is defined as relative density at 15.56 °C as compare with water of the same temperature. The easiest method for measuring the density is by the use of a Anton Paar digital density meter DMA 48 under ASTM D 4052-15 test method.

4.2.2.2 Viscosity analysis

The kinematic viscosity was measured at 40 °C in $m^2 \times s^{-1}$ according to, ASTM D 445 -15a method.

4.2.2.3 Total sulphur analysis

The total sulphur content of the fractions received from it, which are independent on the type of sulphur bond is assumed. The total sulphur can be stated in mg/kg, ppm or % by weight. There are variable sulphur determination methods along with the measuring fundamentals and measuring range. In this study ultraviolet fluorescence method (ASTM D 5453-16^{e1}) was used to determine the total sulphur by Thermo Scientific TS 3000 E Liquid.

4.2.2.4 Pour point analysis

Pour points tell us when the yield point has been reached, i.e. after the formation of paraffin crystal skeleton oil stops flowing. At the cloud point the clouding of oil begins because of the elimination of n-alkane crystals. The cloud point can only be determined for mineral oils which are transparent in layer up to 40 mm thick. This usually does not apply to dark samples. For those dark samples, therefore, the pour point is determined and for the lighter fractions the cloud point described in norms ASTM D 97-16. The pour point result was given in °C.

4.2.2.5 Flash point analysis

ASTM D 93-16a test method was used to determine the flash point by Herzog Pensky-Martens Closed Cup Tester.

4.2.2.6 Calorific value

ASTM D 240-14 test method was used to determine the heat of combustion value by Gallenkamp automatic adiabatic bomb calorimeter.

4.2.2.7 Water content analysis

Water content was determined by Mettler Toledo Coulometric Karl Fischer Titrator, according to study ASTM D 6304-16^{e1} test method

4.2.2.8 Bromine number analysis

ASTM D 1159-07(2012) test method was used to determine bromine number by Mettler Toledo T70 potentiometric titrator.

4.2.2.9 Total acid number analysis

ASTM D 664-11a ^{e1} test method was used to determine total acid number (T.A.N).

4.2.2.10 SIMDIS analysis

The liquid products were analyzed by gas chromatograph with a flame ionization detector (GC-FID) using a Hewlett–Packard 6890 GC. An HP-5 capillary column (30 m length × 0.32 mm diameter coated with cross-linked 5% phenylmethylsiloxane at a thickness of 0.25 mm) was used in the GC system. The cumulative volumes of heavy gas oil, light gas oil, heavy naphtha and light naphtha in the liquid products were determined according to ASTM D2887-16^{a}.

4.2.2.11 FTIR analysis

All infrared spectrums were obtained by using ThermoFisher Nicolet model FTIR spectrophotometer.

4.2.2.12 NMR analysis

Hydrocarbon distribution of liquid products were determined with ^{1}H NMR a "*Varian Mercury AS 400 Plus"* 400 MHz. The distribution of sample is calculated by the following formula ;(Myers, 1975)

$$\text{Aromatics, vol. \%} = \frac{\left(A+\frac{C}{3}\right) \text{x } 10^2}{\left(A+\frac{C}{3}\right)+\left(D+\frac{E}{2}+\frac{F}{3}\right)+B}$$

$$\text{Paraffins, vol. \%} = \frac{\left(D+\frac{E}{3}+\frac{F}{3}\right) \text{x } 10^2}{\left(A+\frac{C}{3}\right)+\left(D+\frac{E}{2}+\frac{F}{3}\right)+B}$$

$$\text{Olefins, vol. \%} = \frac{B \text{ x } 10^2}{\left(A+\frac{C}{3}\right)+\left(D+\frac{E}{2}+\frac{F}{3}\right)+B}$$

A: ring aromatics = 6.6-8.0 ppm

B: olefin = 4.5-6.0 ppm

C : α-methyl = 2.0-3.0 ppm

D: methine (paraffins) =1.5-2.0 ppm

E: methylene (paraffins) =1.0-1.5 ppm

F: methyl (paraffins) = 0.6-1.0 ppm

4.2.2.13 Gas product analysis

The gas products were analyzed by Agilent 7890A gas chromatograph. The system has five valves and three detectors. The FID Channel is configured to analyze the hydrocarbons from C_1 to C_5. The first TCD channel is configured to analyze fixed gases, which may include CO_2, CO, O_2 and N_2. The second TCD channel is dedicated to analyze hydrogen only.

5. RESULTS AND DISCUSSIONS

5.1. Hydrotreating of Canola Oil

In hydrotreating of Canola Oil, two commercial catalysts, Pd/C and $NiMo/Al_2O_3$, were used. The Hydroprocessing experiments with Pd/C catalyst (a hydrogenation catalyst) were carried out under different conditions (the temperatures of 310-375°C for the reaction times of 0 - 60 min. with the initial H_2 pressures of 2-4 MPa). Under the all hydrotreating conditions tested, the waxy product was obtained instead of liquid product. The FTIR spectra of these waxy products showed that no decarboxylation/decarbonylation occurred (Figure 5.1.a).

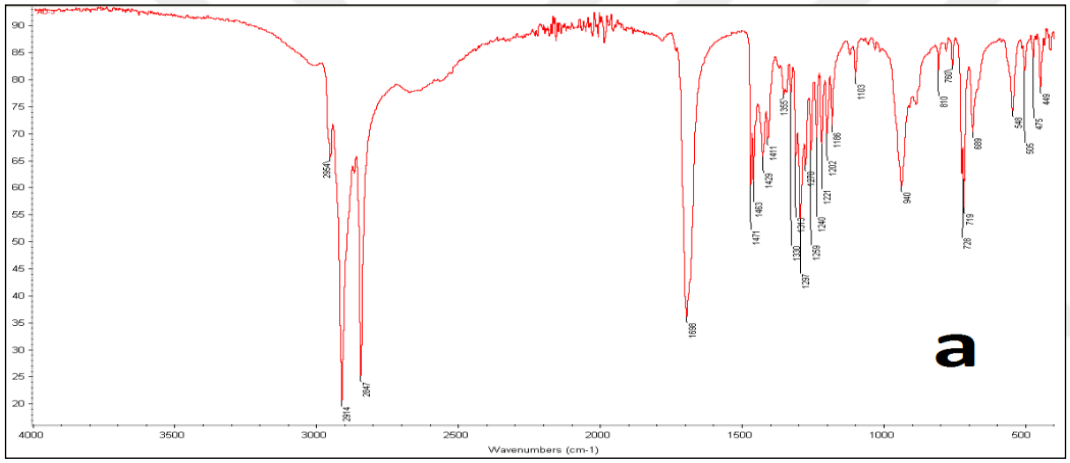


Figure 5.1 FTIR spectra's of the waxy product **(a).** product picture **(b).** (catalyst: Pd/C, temperature: 375 °C, initial H_2 pressure: 3 MPa, reaction time: 60 min.)

Because of this, following reactions were done with $NiMo/Al_2O_3$ catalyst. In hydroprocessing with $NiMo/Al_2O_3$, the affects of temperature, reaction time and initial H_2 pressure on liquid yield were investigated.

5.1.1 Initial hydrogen pressure effect

To examine the influence of initial hydrogen pressure on the liquid yield, a series of experiments with different hydrogen pressure at 400 °C for a reaction time of 60 min. were carried out. As expected, an increase in partial H_2 pressure decreased the liquid yield.

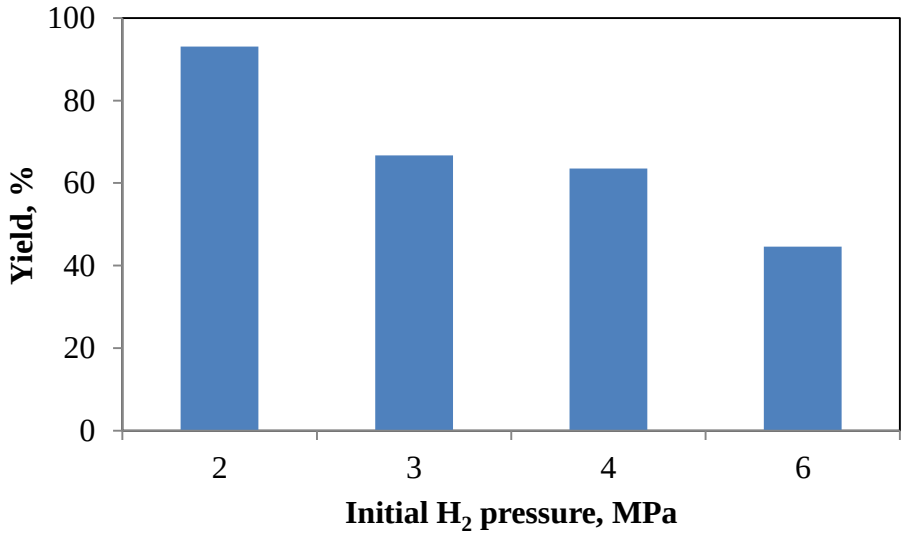


Figure 5.2 The effect of initial H_2 pressure on liquid yield

The yield decreased from 93.7 % to 66.7 % as the pressure rising up from 2 to 3 MPa (Figure 5.2). This can be explained in that 2 MPa of hydrogen pressure is not enough to reduce the triglycerides via C–O bond hydrogenolysis. The similarity of FTIR spectras (not shown here) of canola oil and liquid obtained with 2 MPa of H_2 supports this idea. There was no prominent difference in liquid yield as the initial H_2 pressure was rised up from 3 to 4 MPa. Even if, increasing pressure above 4 MPa, liquid yield significantly decreased again. This shows that high H_2 pressures enhance the cracking reactions besides HDO, and decarboxylation/decarbonylation reactions.

5.1.2. Effects of reaction temperature and reaction time

Figure 5.3 indicates the liquid product yields for hydroprocessing of canola oil using an initial H_2 pressure of 3 MPa as a function of temperature and reaction time.. The temperature affect on liquid yield was observed mainly above 400 °C. Similarly, the affect of reaction time also varied depending on the temperature. In the case of hydroprocessing at high temperatures above 350 °C, reaction time increasing caused liquid yield decreasing. It is plausible that higher reaction temperatures and reaction times resulted in cracking of liquid products to gaseous products.

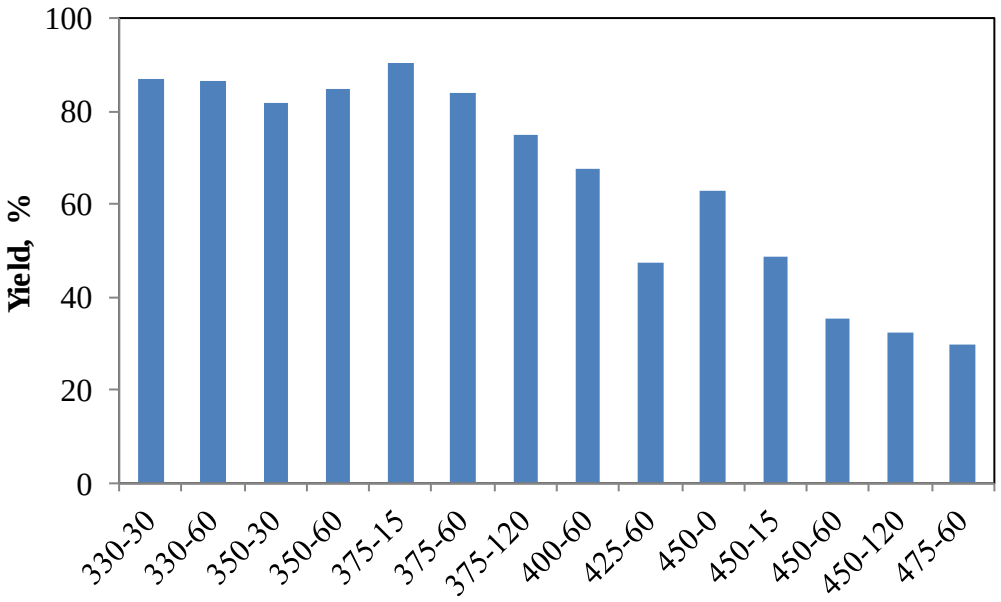


Figure 5.3 Effect of reaction temperature and time on liquid yield obtained from hydroprocessing of canola oil with $NiMo/Al_2O_3$ catalyst.

As seen from Figure 5.4, the high temperature promotes cracking reactions resulted in formation of hydrocarbon gasses. CO and CO_2 percent decreased 71 to 40 % when the reaction temperature increased 375 to 450°C. The results showed that as the reaction temperature increased, the decarbonylation/decarboxylation ratio decreased. Interestingly, at 450 °C, the CO_2 amount was higher than CO. The reason is not only the fact that the rate of decarboxylation was higher than that of decarbonylation. Probably, the reactions between the CO/CO_2 and the hydrogen (such as water-gas shift and methanation) were occurred (Galadima and

Muraza, 2015; Arun et al., 2015). These reactions led to the consumption of CO and production of CO_2 and CH_4. The catalytic effect of catalyst on the gas composition can be seen by comparison of run 450-NiMo and run 450-T. In the case of thermal run, CO and CO_2 yields are almost relatively equal. This shows that $NiMo/Al_2O_3$ catalyst had catalytic effect on water-gas shift and methanation.

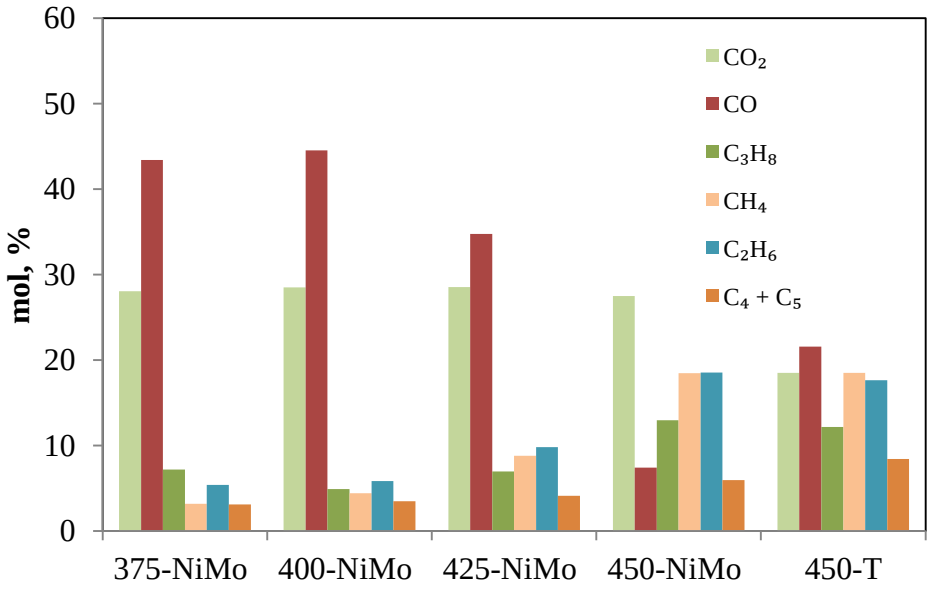


Figure 5.4 Gas composition from hydrotreating of canola oil in the presence of $NiMo/Al_2O_3$ (reaction time: 60 min; initial H_2 pressure: 3 MPa; 450- T: thermal process at 450 °C)

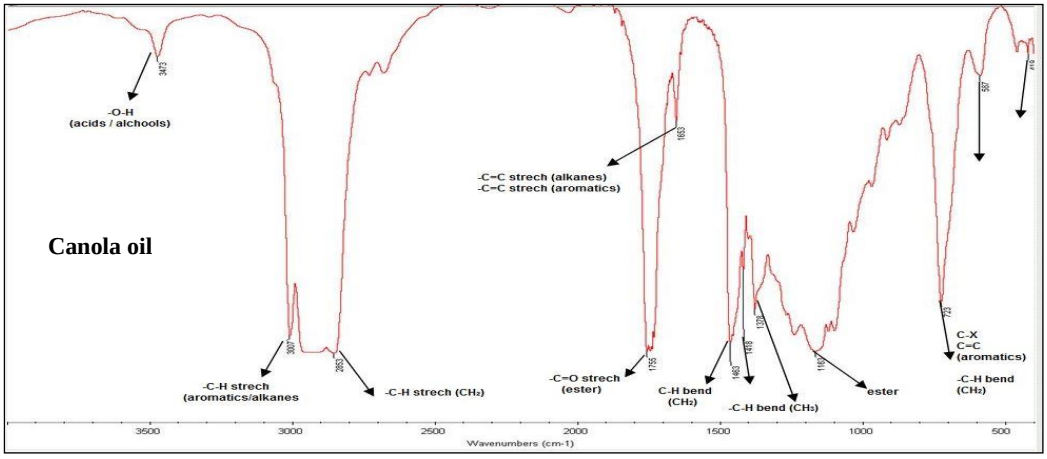
The liquid products were analyzed by Fourier transform infrared spectroscopy (FTIR) analysis was used to check the functional groups in liquid products. The results are represented in Figure 5.5. For comparison purpose, FTIR spectra of canola oil and commercial diesel are also given in Figure 5.5

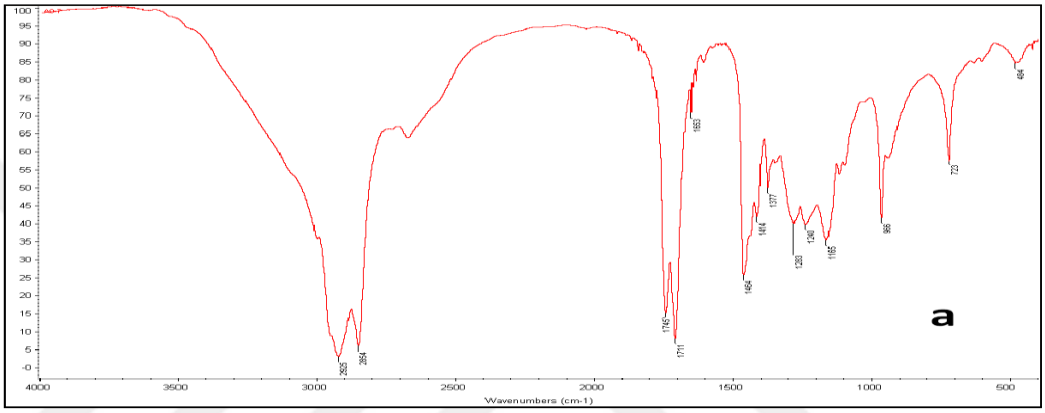
In the FTIR spectra of canola oil, the band at 3473 cm^{-1} is assigned to –OH functional group of carboxylic acids and the large peaks at 1163cm^{-1} and 1755 cm^{-1} are typical for esters. These peaks become less predominate as increasing of temperature. The peak at 1711 cm^{-1} shows the formation of intermediate acids (Nimkarde and Vaidya, 2016). At the highest temperature (450 °C), the bands corresponding to carboxylic acids and esters disappeared. The spectra of liquid product (Fig.5.5.e) are almost similar with the spectra of commercial diesel. From

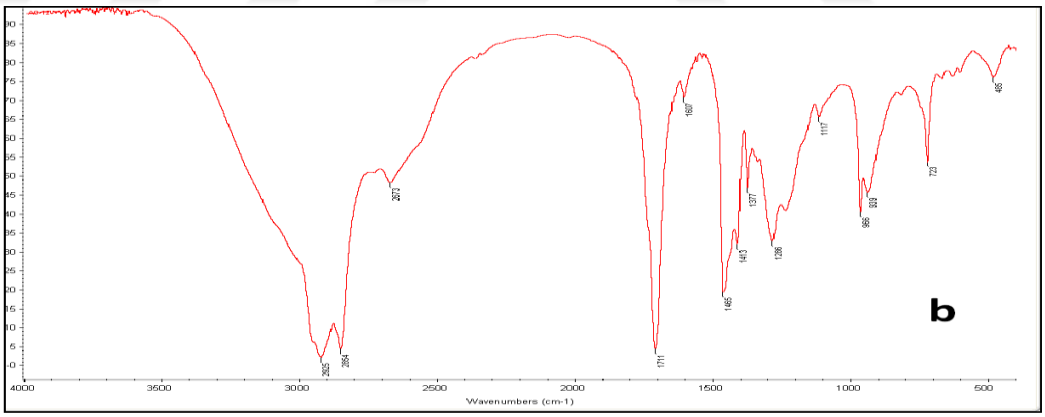
the comparison of the FTIR spectra in Figure 5.5.e. and f., it is clearly understood that the role of the NiMo catalyst in conversion of glycerides to hydrocarbons is also crucial, as well as temperature.

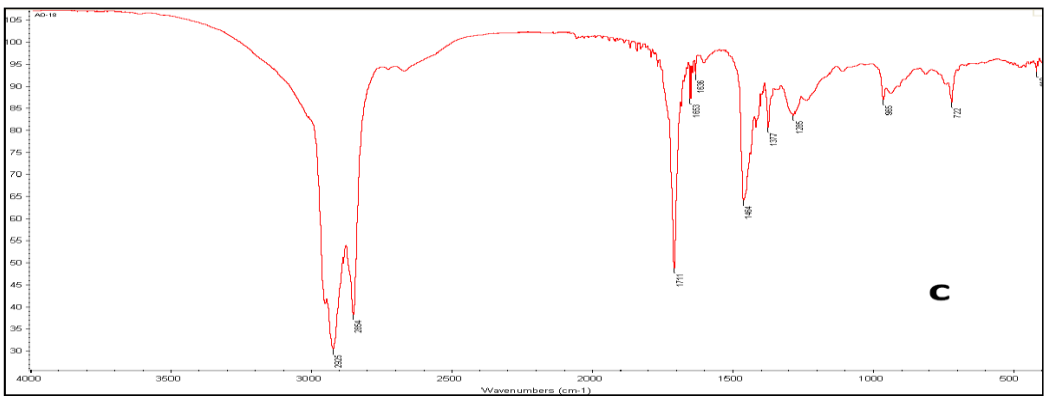
The reaction time has also effect on the conversion of glycerides. Even at 450 °C, the peak at 1711 cm^{-1} corresponding to intermediate acids are present in liquid spectra for the reaction time less than 60 min. (Figure 5.6).

The fact that acid value of liquids decreased from 144.6 to 4.0 mg KOH/ g when the temperature rised up 375 to 450 °C also indicates the decrease in intermediate acids with hydrotreating temperature (Table 5.1).


Canola oil
-O-H
(acids / alchools)
-C-H strech
(aromatics/alkanes
-C-H strech (CH₂)
-C=C strech (alkanes)
-C=C strech (aromatics)
-C=O strech
(ester)
C-H bend
(CH₂)
-C-H bend (CH₃)
ester
C-X
C=C
(aromatics)
-C-H bend
(CH₂)
Wavenumbers (cm-1)


a
Wavenumbers (cm-1)


b
Wavenumbers (cm-1)


c
Wavenumbers (cm-1)

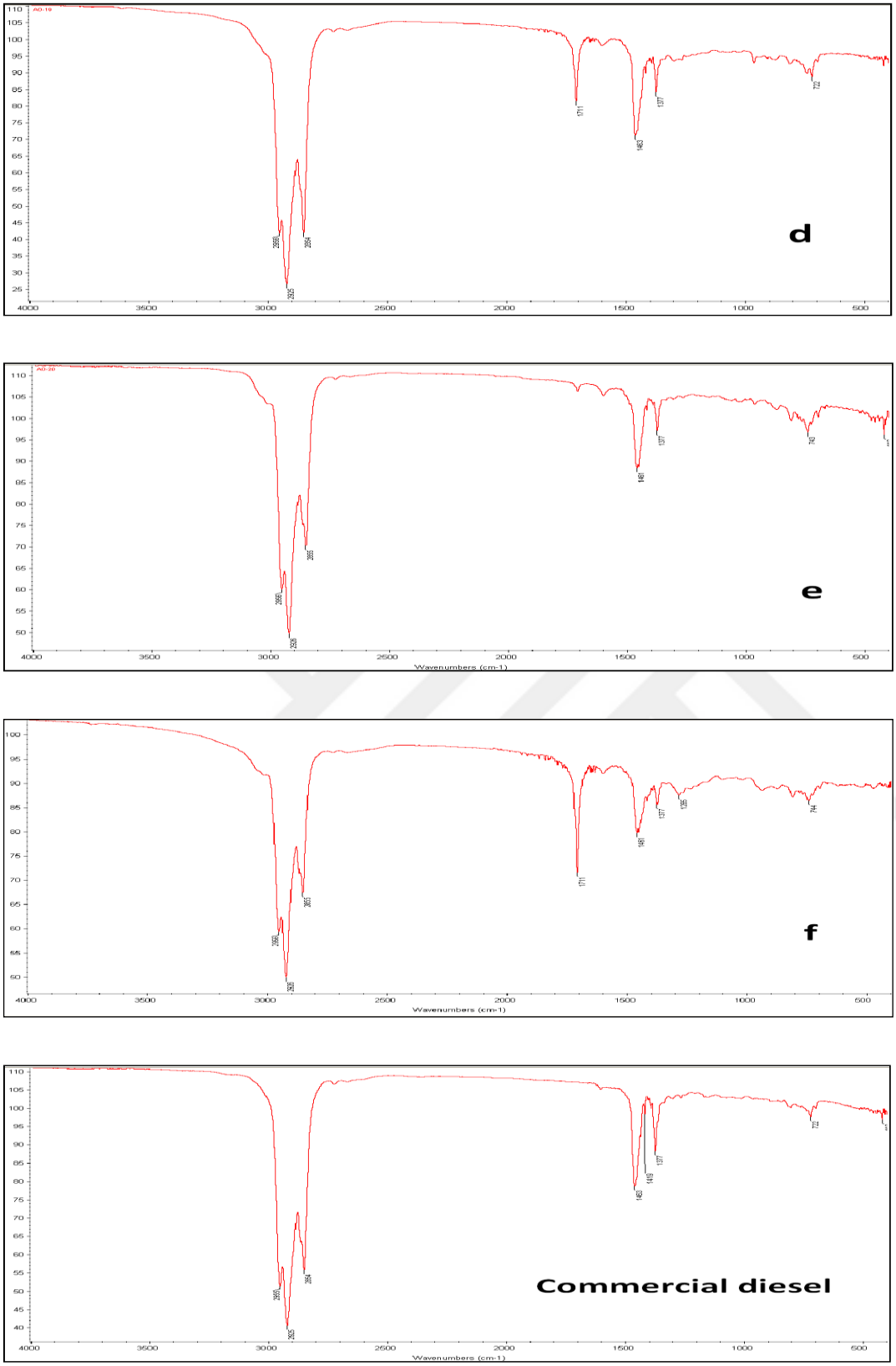


Figure 5.5 FTIR spectras of canola oil, commercial diesel and liquid products obtained in the presence of NiMo at 350 °C **(a)**, 375 °C **(b),** 400 °C **(c)**, 425 °C **(d),** 450 °C **(e)** and liquid product obtained in the absence of catalyst at 450 °C **(f)**. (Initial H_2 pressure: 3 MPa; reaction time: 60 min.)

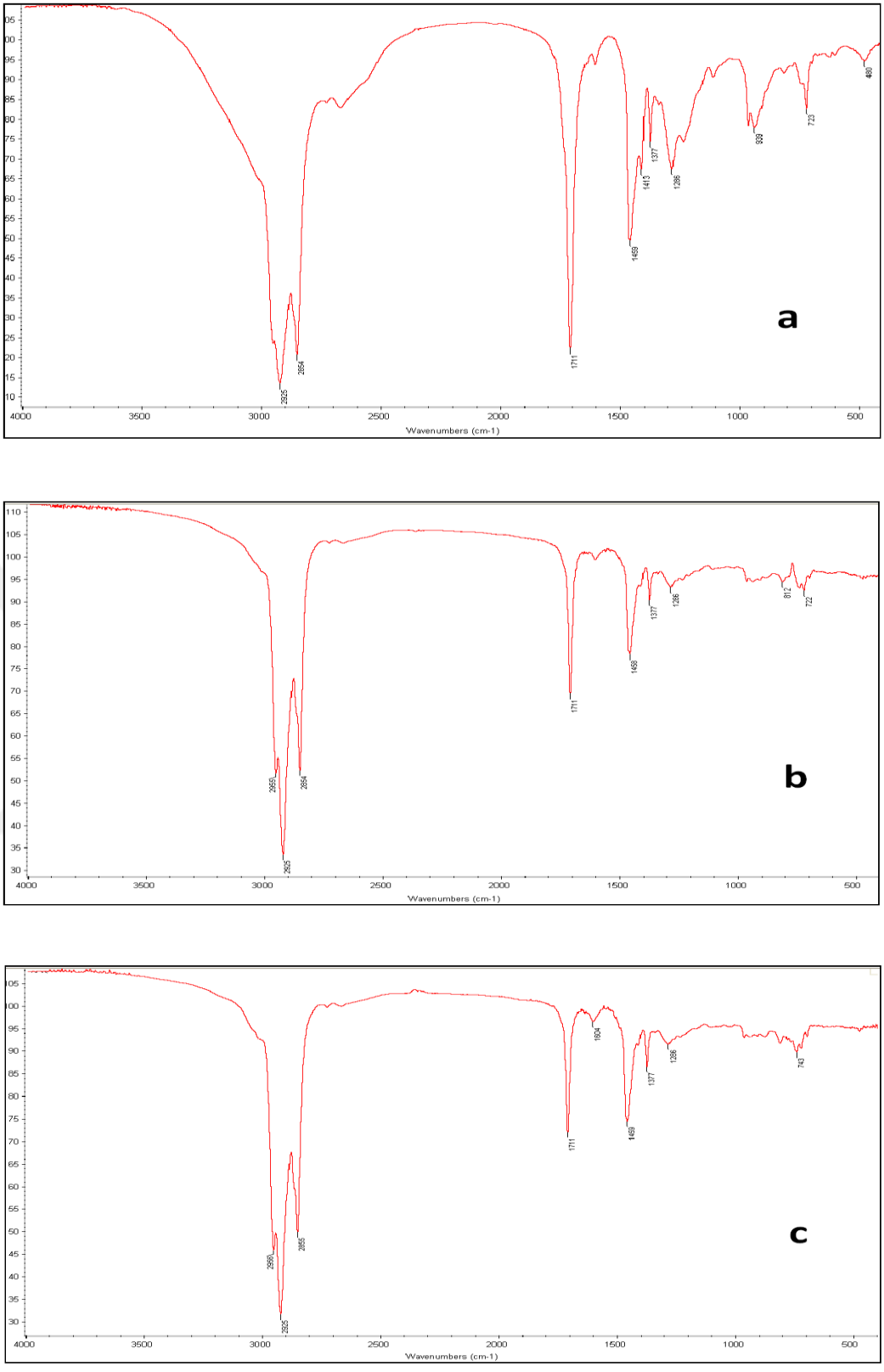


Figure 5.6. FTIR spectras of liquid products obtained in presence of NiMo for the reaction times 0 min **(a),** 15 min. **(b),** 30 min **(c)** (Initial H_2 pressure: 3 MPa; reaction temperature: 450 °C).

The degree of unsaturation of liquids was determined by bromine number analysis. By increasing of temperature, bromine number value decreased from 35.09 g to 27.30 g Br_2/100 g. Generally, at high temperatures with hydrogen, the fatty acyl chains turn into saturated and/or following decarboxylation, decarbonylation and hydrogenation reactions producing saturated hydrocarbons. (Simacek et al. 2010) studied the hydrotreating of canola oil at 360 °C and 7 MPa using a mercantile Ni–Mo/Al_2O_3 catalyst, the product obtained was a solid form containing *n*-heptadecane and *n*-octadecane with low concentrations of other *n*-alkanes and *i*-alkanes. In contrast, we produced liquid product containing olefins and aromatics besides paraffins (Table 5.1). We can say that enhanced reaction temperatures favor catalytic cracking reactions besides saturation, decarboxylation and decarbonylation.

In this study, hydrocarbon types of the liquid products were analyzed with ^{1}H NMR methods. In catalytic runs, although the amount of aromatic hydrocarbons was independent in temperature, saturation of olefin increased as increasing of temperature. By comparing the results from both thermal and catalytic runs, it is clear that catalyst inhibited the aromatization during hydroprocessing.

Table 5.1 The effect of reaction temperature on some properties of liquids obtained from hydroprocessing of canola oil with and without catalyst. (Initial H_2 pressure: 3 MPa; reaction time: 60 min).

	density at 15°C, g/cm^3	Br number, g/100 g	T.A.N, mg KOH/ g	Hydrocarbon types, vol %		
				Paraffins	Olefins	Aromatics
Canola oil	0.9202	60.5	0.07	-	-	-
375 - NiMo	0.9123	35.1	144.60	62.03	24.99	12.98
400 - NiMo	0.8835	28.5	66.60	74.14	13.93	11.92
425 - NiMo	0.8608	27.5	32.80	71.69	13.49	14.82
450 - NiMo	0.8502	27.3	4.00	80.77	5.51	13.72
450 - Thermal	0.8814	23.8	52.50	64.82	10.7	24.47

5.1.3 Comparison of hydrotreated canola oil with commercial diesel

The simulated distillation curves of liquids from catalytic and non-catalytic hydrotreating at 450 °C are given in Figure 5.7. To compare the simulated distillation curves of traditional diesel and gasoline are also given. The fractions of liquids were classified as naphtha (<204 °C), light gas oil (204-343 °C) and heavy gas oil (>343 °C) according to petroleum fractions. The liquid from catalytic run contained about 60 % naphtha fraction (boiling point range <172 °C) and 40 % light gas oil fraction (172 °C <B.P. <232 °C), while naphtha and light gas oil fractions were approximately 40 % and 60 % in liquid from thermal run.

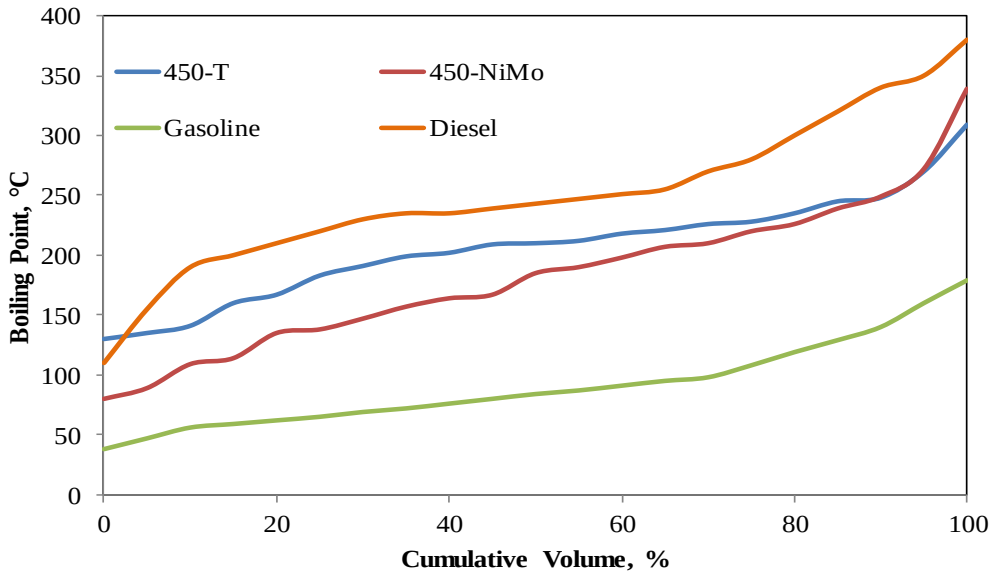


Figure 5.7 Simulated distillation curves of liquids from hydrotreating at 450 °C with an initial H_2 pressure of 3 MPa for 60 min. and of commercial diesel and gasoline liquids.

The fuel characteristic of hydrotreated canola oil at 450 °C in the presence of NiMo catalyst is comparatively given in Table 5.2. The main disadvantage of renewable diesel is poor cold flow property. However, in this study we produced renewable diesel has high cold flow property. The pour point of hydrotreated canola oil is lower, even, than commercial diesel. As can be understood that hydrotreated canola oil is a mix of different petroleum fractions, is not consisted of diesel fraction only. Hydrotreated canola oil should be further distillated into gasoline and diesel fractions.

Table 5.2 Fuel specifications of canola oil, hydrotreated canola oil and commercial diesel

Test	Unit	Canola Oil	Hydrotreated Canola Oil	Commercial Diesel	Method
Density at 15 °C,	g/cm³	0.9202	0.8502	0.8200.845	ASTM D-4052-15
Kinematic Viscosity at 40 °C	cSt	34.0	2.8	2.0-4.5	ASTM D-445-15a
Flash Point	ºC	> 310	< 30	55 Min	ASTM D-93-16a
Pour Point	°C	-21	-35	-18	ASTM D-97-16
Bromine Numbers	g/100g	60.5	27.3	< 1	ASTM D-1159-07
Water	mg/kg	505	685	200 Max	ASTM D-6304-16^{e1}
Sulfur	mg/kg	5.0	3.7	10 Max	ASTM D-5453-16^{e1}
Heat of Combustion	MJ/kg	46.3	44.6	46	ASTM D-240-14
Total Acid Number	mg KOH/g	< 0.1	4.0	0.5 Max	ASTM D-664-11a^{e1}

5.2. Co-processing of Canola Oil with HVGO

Another approach in green diesel production is co-processing of vegetable oils/fats with a conventional feedstock in existing hydrocracking plant. Co-processing is a promising option to integrate the conversion process in existing refineries. The aim of this study was to examine the process ability of canola oil in existing hydrocracking plant

For this purpose, hydrocracking of the mixture of canola oil in HVGO at the ratio of 20 wt. % was made with and lack of a commercial hydrocracking catalyst (DHC-8) at three different temperatures (400-450 °C). To monitor the affect of canola oil on hydrocracking process, HVGO and canola oil alone was also hydrocracked thermally and in the presence of DHC-8. The ideal reaction terms for hydrocracking process were defined by the pre-experiments with HVGO. These terms were 6 MPa initial hydrogen pressure, 60 minute reaction period and catalyst amount of 10 wt. %.

In the case of hydrocracking of canola oil by itself, liquid yield decreased from 73 % to 52 %, as the reaction temperature increased. The use of catalyst had no significant affect on liquid yield. As in the hydrotreating with $NiMo/Al_2O_3$ catalyst, temperature and catalyst enhanced decarboxylation/decarbonylation reactions as well as cracking reactions resulting in formation of hydrocarbon gasses.

The FTIR spectra of the liquid obtained at 450 °C in catalytic run shows to complete conversion of initial triglycerides, no peaks correspondent to carboxylic acids and esters (Figure 5.8.c).

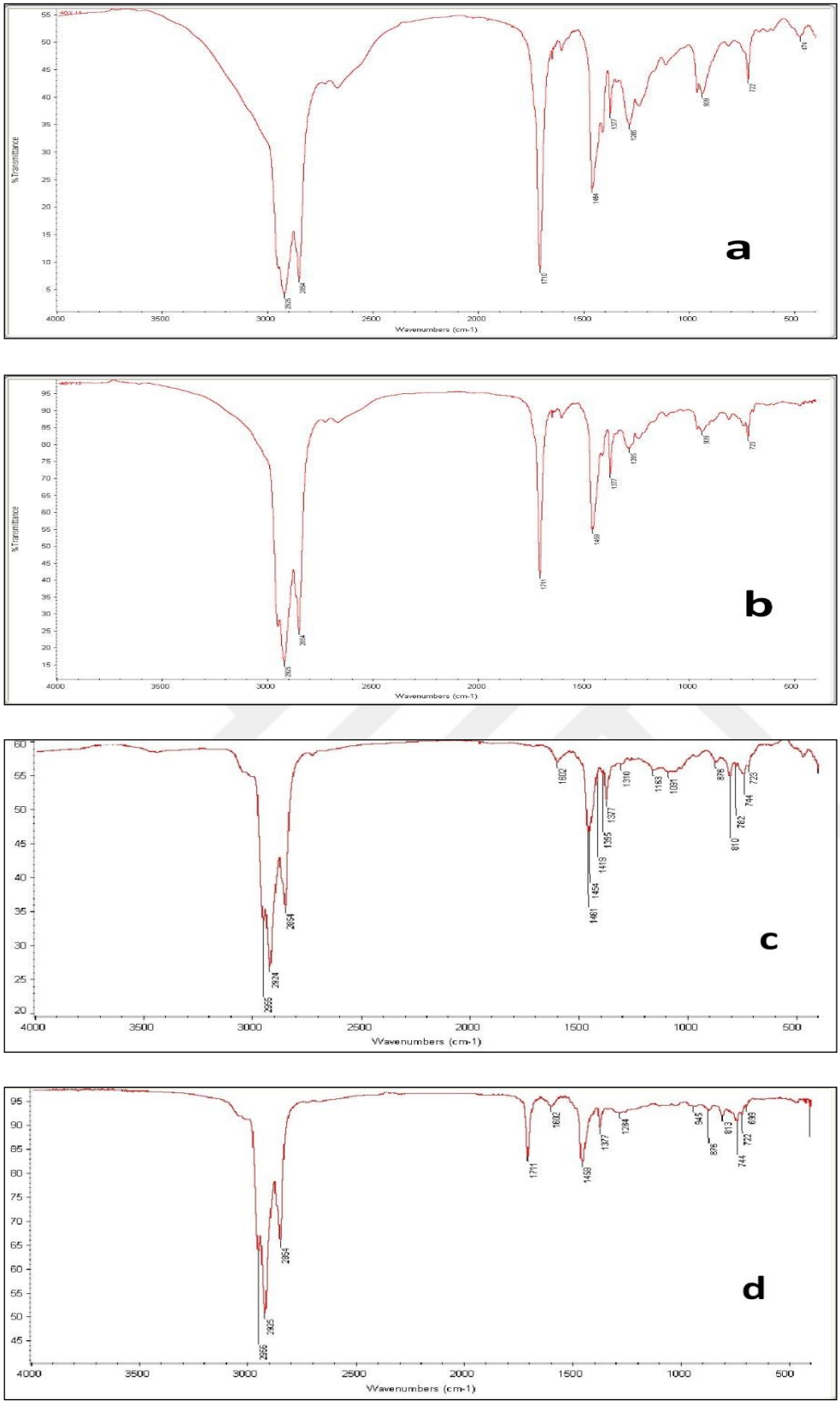


Figure 5.8 FTIR spectras of liquid products obtained from canola oil in the presence of DHC-8 at the temperatures of 400 °C **(a),** 425 °C **(b),** 450 °C **(c)** and absence of catalyst **(d).** (Initial H_2 pressure: 6 MPa; reaction time: 60 min.)

Figure 5.9 shows the liquid yield from the hydrocracking of blend and HVGO at different temperatures without catalyst and with DHC-8 catalyst. Liquid samples were called as subsequent the ‘‘feedstock type-reaction temperature – catalyst- ’’ series (e.g. HVGO-400-T stands for hydrotreating of HVGO at 400 °C without of catalyst). As expected, liquid yield decreased with increasing temperature for both HVGO and blend. In hydrocracking of HVGO, the effect of catalyst on liquid yield varied with temperature. At the temperatures below 450 °C, the catalytic effect was more occurred, so liquid yields off catalytic studies were inferior than that from thermal run. When the temperature was 450 °C, both thermal and catalytic reactions happen meanwhilso liquid yields from both thermal and catalytic studies were almost similar, 56 % and 54 %, respectively.

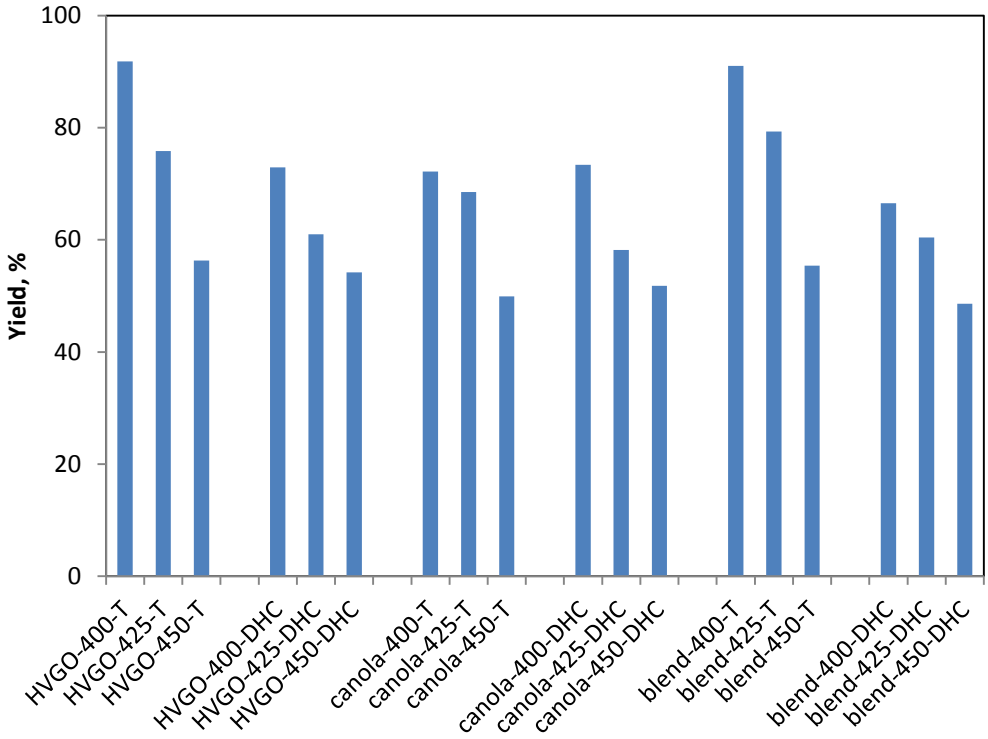


Figure 5.9 Effect of reaction temperature on liquid yield obtained from hydrocracking of heavy vacuum gas oil, canola oil and their blend in the absence and presence of DHC-8 catalyst.

As seen Figure 5.9, liquid yields from both thermal and catalytic hydrocracking of canola oil at 450 °C were also same. However in the case of

hydrocracking of the mixture, liquid yield obtained from catalytic run at 450 °C were lower than from thermal run at 450 °C. And also experimental liquid yield from catalytic hydrocracking was lower than the predicted one. This indicates as the existence of canola oil effected the cracking of HVGO at 450 °C. High activity of unsaturated hydrocarbons which constitute the prime intermediate products of canola oil hydrocracking decreased the yield of liquid products (Doronin et al., 2013).

In hydrocracking at temperature of 400 °C, about 50 % of the gas products were CO_x, due to the decarbonylation/decarboxylation of canola oil (Figure 5.10). As increasing temperature, hydrocarbon gases become more dominant, indicating the increased in formation of gases from cracking of HVGO.

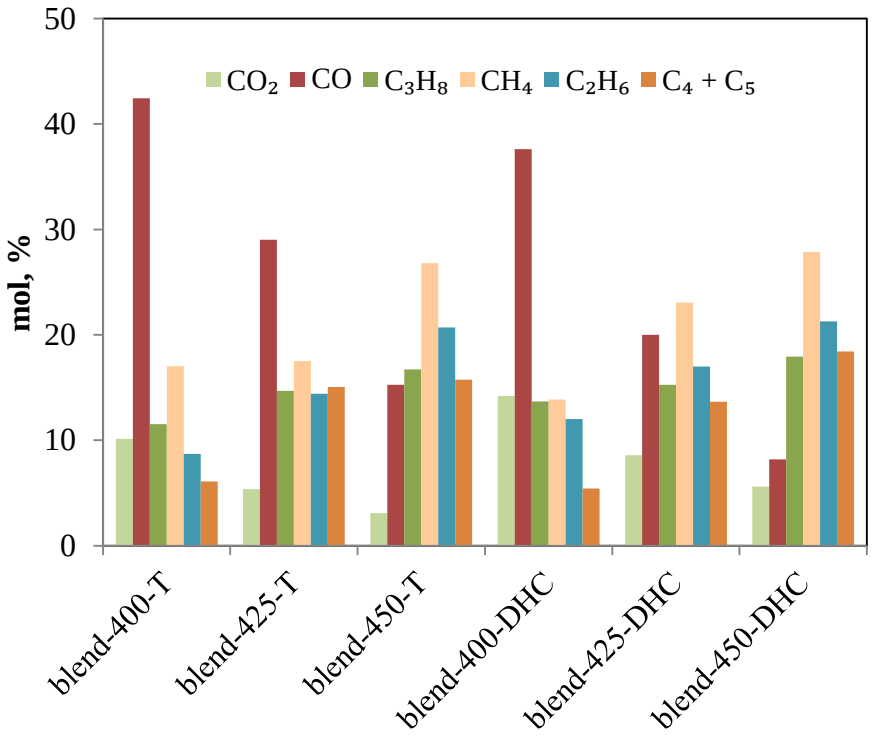


Figure 5.10 Gas compositions from hydrocracking of the canola/HVGO blend in presence and the absence of DHC-8 catalyst. (initial H_2 pressure: 6 MPa; reaction time: 60 min).

The simulated distillation curves of liquids obtained from both HVGO and the HVGO/canola blend without of catalyst and with catalyst are given in Figure 5.11 and Figure 5.12.

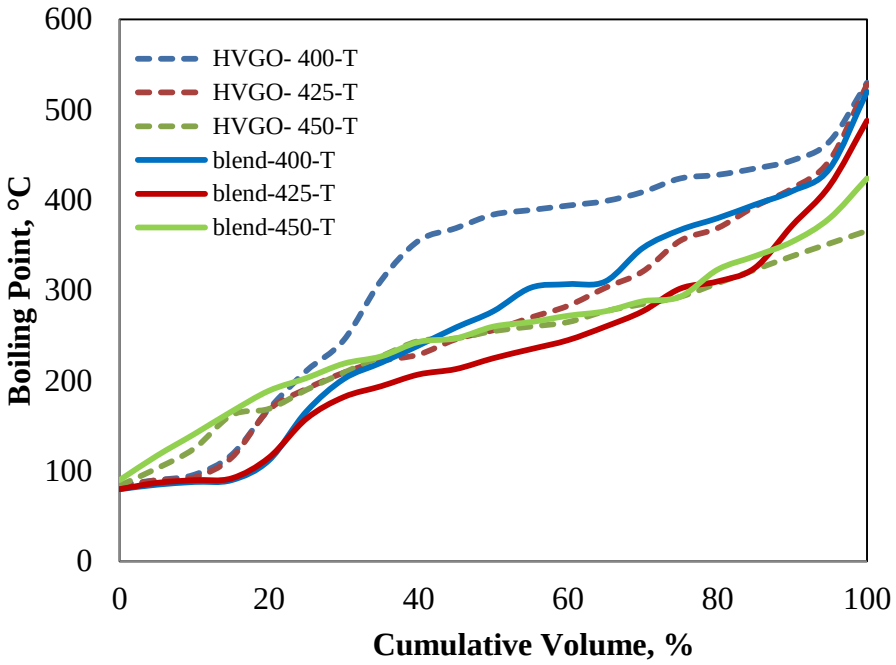


Figure 5.11 Simulated distillation curves of liquids obtained from thermal hydrocracking of HVGO and canola/HVGO blend at different temperatures

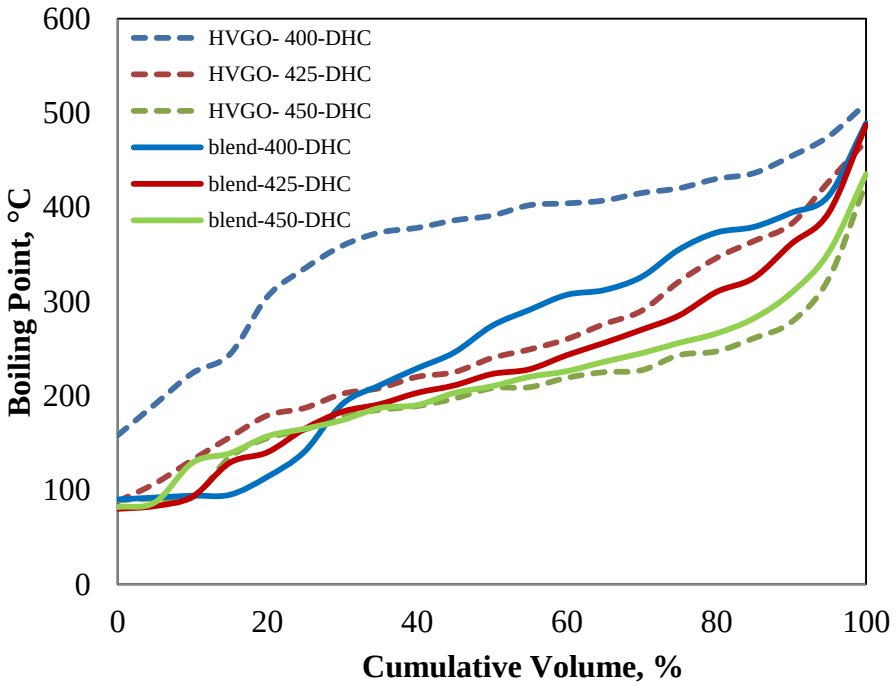


Figure 5.12 Simulated distillation curves of liquids obtained from catalytic hydrocracking of HVGO and canola/HVGO blend at different temperatures

The main effect of the addition of canola into HVGO on the boiling point distribution of liquids was watched at lower temperature hydrocracking (at 400 °C). In both cases thermal and catalytic studies, the liquid obtained whence blend contained lighter compounds whence that from HVGO alone. It should be noted that during hydrocracking of canola oil alone at 400 °C, liquid contained lighter compounds as compared to HVGO hydrocracking Figure 5.13.

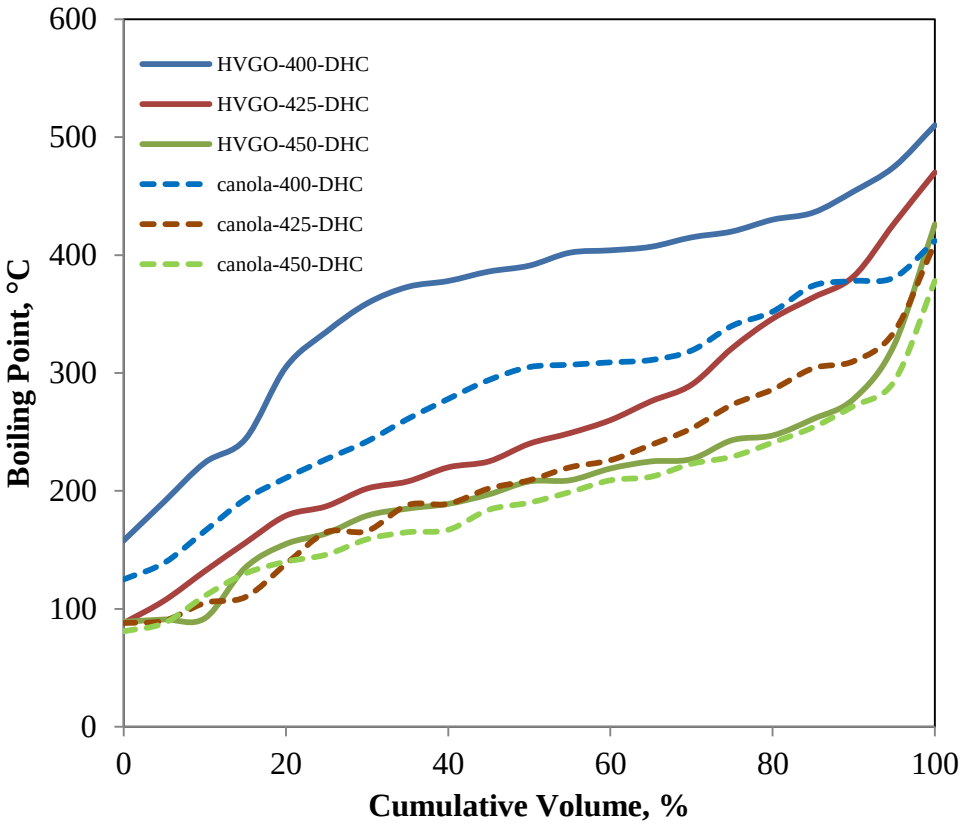


Figure 5.13 Simulated distillation curves of liquids obtained from catalytic hydrocracking of HVGO and canola at different temperatures

The using of catalyst lead to formation lighter compounds. The liquid from catalytic run at 450 °C contained about 45 wt.% naphtha and 47 wt.% light gas oil, whereas naphtha and light gas oil fractions were about 25 wt.% and 61 wt.% in liquid from thermal run. The addition of canola into HVGO also affected the hydrocarbon types in liquid product. The hydrocarbon types in liquids obtained from thermal and catalytic hydrocracking of HVGO/canola blend, HVGO and canola at 450 °C are presented in Figure 5.14.

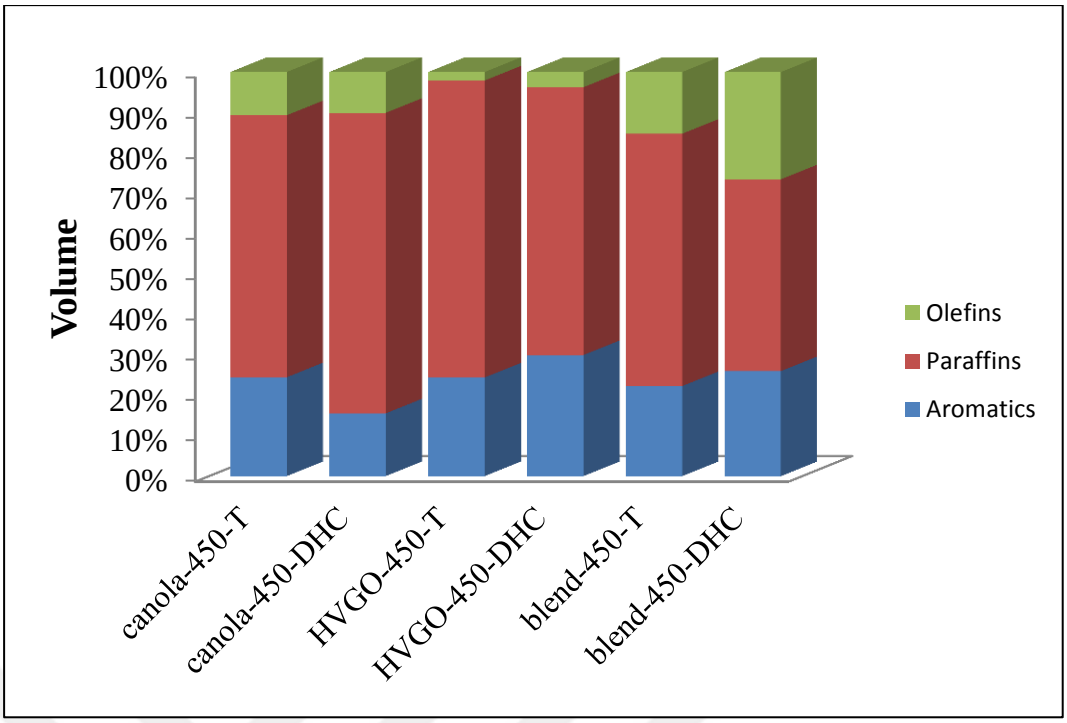


Figure 5.14 Hydrocarbon types in liquids obtained from hydrocracking at 450 °C. (Initial H_2 pressure: 6 MPa; reaction time: 60 min.)

Adding canola oil to HVGO, olefin content remarkably increased while paraffin content decreased. The olefin content of liquid was extremely higher than the predicted one. It is clear that interaction between degradation products from HVGO and canola oil increased the formation of olefins. On the other hand, canola oil addition didn't influence aromatic content of liquid product. This may be associated with presence of hydrogen. Because, it was reported that, in case of cracking in the absence of hydrogen, conversion of vacuum gas oil was enhanced through aromatization by the promoting effect of olefins in vegetable oil (Doronin et al., 2013) .

5.3 Co-processing of Waste Cooking Oil with HVGO

In this study, we have also carried out hydrocracking of HVGO containing waste cooking oil (WCO). The waste oil provided from a local restaurant. The mixture having 20 wt.% WCO was hydrocracked with DHC-8 catalyst at 450 °C and 6 MPa initial H_2 pressure. The liquid yield obtained from WCO/HVGO blend was 56 wt.%, which was slightly higher than from canola/HVGO blend (49

wt.%). More interesting is that the liquid contained 72 wt.% naphtha fraction, 74.2 wt.% paraffinic and 9.3 wt.% olefinic hydrocarbons. The simulated distillation curve of liquid acquired off WCO/HVGO blend with DHC-8 catalyst is given in Figure 5.15. For comparing, the simulated distillation curves of liquids acquired off both HVGO and the canola/ HVGO blend in the presence of DHC-8 are also given in Figure 5.15.

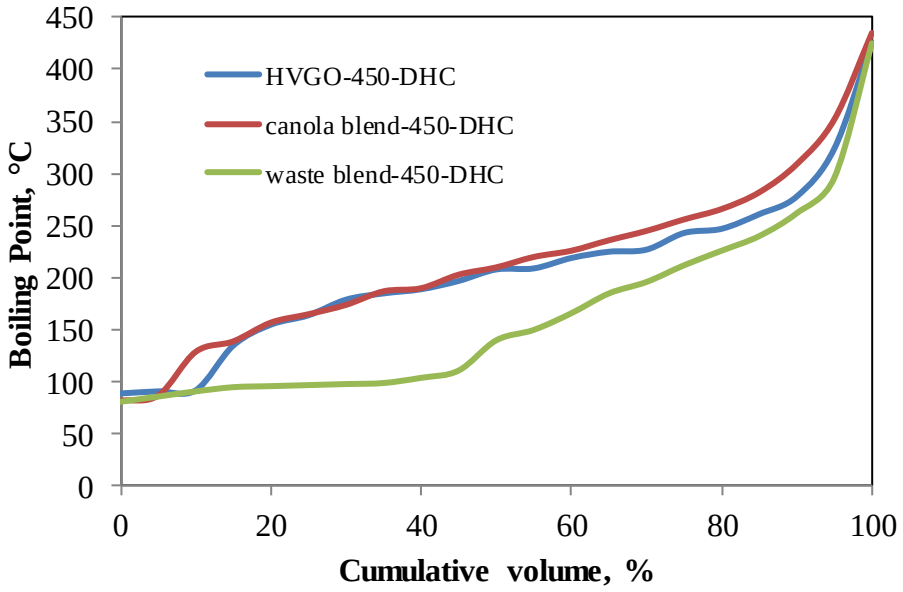


Figure 5.15 Simulated distillation curves of liquids obtained from catalytic hydrocracking of HVGO, canola/ HVGO blend and WCO/HVGO blend. (Initial H_2 pressure: 6 MPa; reaction time: 60 min.)

No peaks correspondent to functional groups of carboxylic acids and esters were observed in FTIR spectra of liquid product obtained from blend containing WCO (Figure 5.16). This shows that waste oil was completely converted into hydrocarbons. The fact that acid value of liquid was 2.8 mg KOH/ g, it indicates the presence of less amount intermediate acids, which are intermediate products of ester degradation.

It should be noted that hydrocracking of WCO/HVGO blend produced liquid product containing more paraffinic hydrocarbon than HVGO alone and canola/HVGO blend (Figure 5.17).

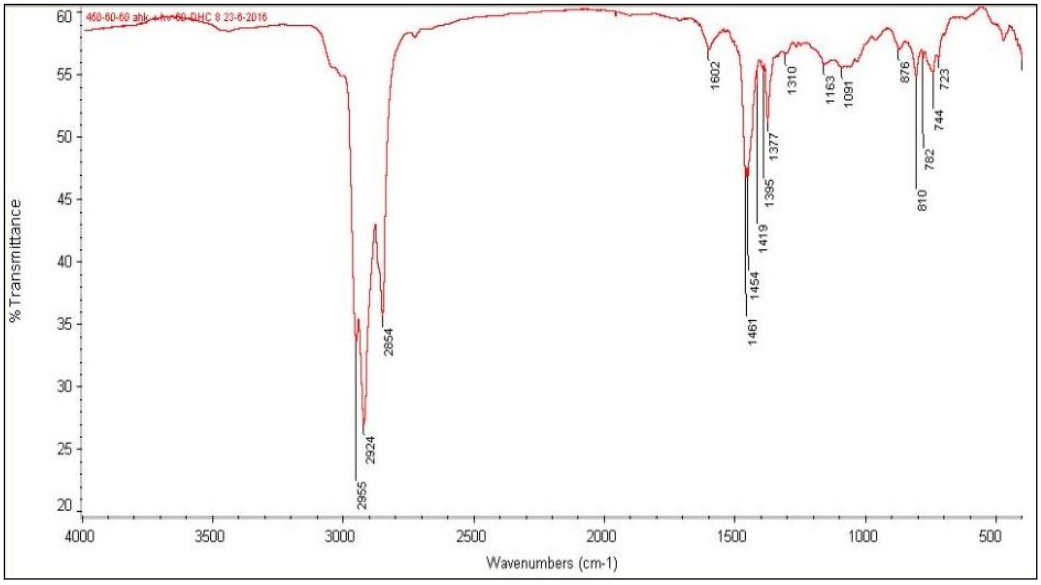


Figure 5.16 FTIR spectras of liquid product obtained from WCO/HVGO blend in the presence of DHC-8 at 450 °C. (Initial H_2 pressure: 6 MPa; reaction time: 60 min.)

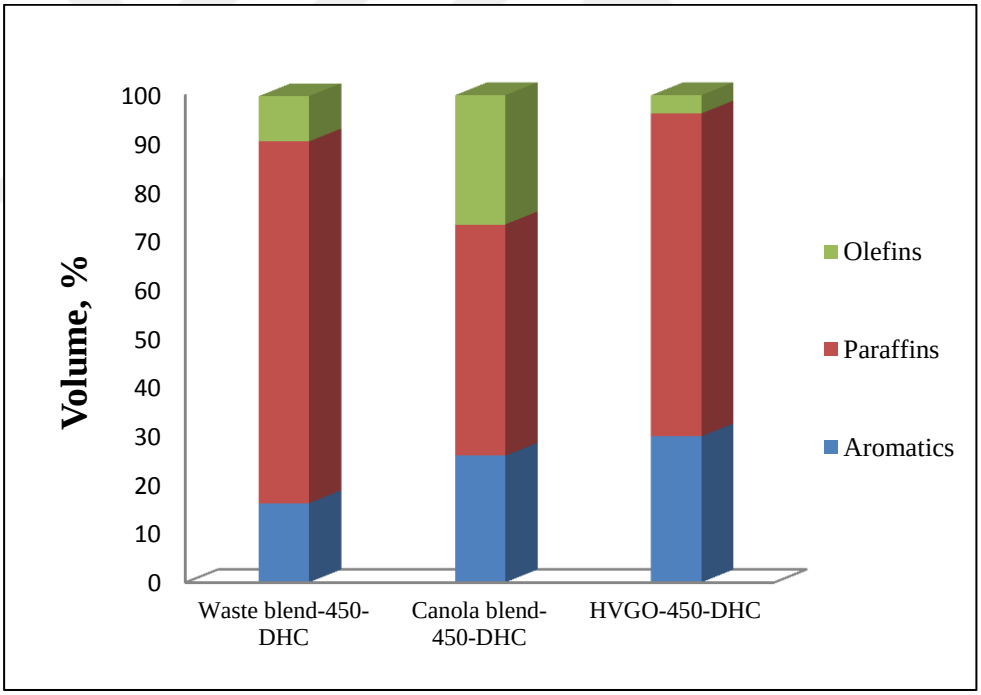


Figure 5.17 Hydrocarbon types in liquids obtained from WCO/HVGO, canola/HVGO and HVGO in the presence of DHC-8 at 450 °C. (Initial H_2 pressure: 6 MPa; reaction time: 60 min.)

6. CONCLUSION

In this study, conversion of canola oil, as a renewable source, into petroleum fuels using existing refinery processes was investigated. For this purpose, hydrotreating of canola oil and hydrocracking of canola oil/HVGO mixture were performed. The effect of catalyst, temperature, reaction time and hydrogen pressure on the efficiency and properties of products were examined.

We obtained the following results from our experiments.

- In the case of hydrotreating of canola oil, high H_2 pressures, temperature and catalyst enhance the cracking reactions besides HDO, and decarboxylation/decarbonylation reactions. The $NiMo/Al_2O_3$ catalyst inhibited the aromatization during hydroprocessing. When the temperature of reaction rised up, decarbonylation /decarboxylation ratio decreased.

- The hydrotreating of canola oil with $NiMo/Al_2O_3$ catalyst at 450 °C for a reaction time of 60 min. with an initial H_2 pressure of 3 MPa yielded a liquid product having petroleum hydrocarbons. The liquid yield obtained under this condition was 35 wt.%. The liquid product contained about 60 wt.% naphtha fraction and 40 wt.% light gas oil fraction.

- In the case of hydrocracking of canola oil by itself, liquid yield decreased as the increasing of reaction temperature. The use of catalyst had no considerable effect on liquid yield. The temperature and catalyst enhanced decarboxylation/decarbonylation reactions as well as cracking reactions resulting in formation of hydrocarbon gasses. The hydrocracking of canola oil in the presence of DHC-8 catalyst at 450 °C for a reaction time of 60 min. with an initial H_2 pressure of 6 MPa yielded a liquid product having petroleum hydrocarbons. The liquid yield obtained under this condition was 52 wt.%. The liquid product contained about 42 wt.% naphtha fraction and 34 wt.% light gas oil fraction.

- In case of hydrocracking of canola oil /HVGO (20/80), the presence of canola oil affected the cracking of HVGO at 450 °C. experimental liquid yield from catalytic hydrocracking was lower than the predicted one. The addition of canola into HVGO also affected the hydrocarbon types in liquid product. Adding canola oil to HVGO, olefin content remarkably increased while paraffin content decreased. The olefin content of liquid was extremely higher than the predicted one.

- No peaks correspondent to functional groups of carboxylic acids and esters were observed in FTIR spectra of liquid product obtained from blend (hydrocracking of canola oil/HVGO at 450 °C).

- The studies in this thesis showed that canola oil could be converted into petroleum hydrocarbons by refinery processes.

REFERENCES

ASTM D93-16a Standard test methods for flash point by Pensky-Martens closed cup tester.

ASTM D97-16 Standard test method for pour point of petroleum products.

ASTM D240-14 Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter.

ASTM D445-15a Standard test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity).

ASTM D664-11a^{e1} Standard test method for acid number of petroleum products by potentiometric titration.

ASTM D975-16a Standard specification for diesel fuel oils

ASTM D1159-07(2012) Standard test method for bromine numbers of petroleum distillates and commercial aliphatic olefins by electrometric titration

ASTM D2887-16a Standard test method for boiling range distribution of petroleum fractions by gas chromatography

ASTM D4052-15 Standard test method for density, relative density, and API gravity of liquids by digital density meter

ASTM D5453-16^{e1} Standard test method for determination of total sulfur in light hydrocarbons, spark ignition engine fuel, diesel engine fuel, and engine oil by ultraviolet fluorescence

ASTM D6304-16^{e1} Standard test method for determination of water in petroleum products, lubricating oils, and additives by coulometric Karl Fischer titration

ASTM D6751-15c^{e1} Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels

ASTM D7169-16 Standard test method for boiling point distribution of samples with residues such as crude oils and atmospheric and vacuum residues by high temperature gas chromatography

Arun, N., Sharma, R., V., Dalai, A., K., 2015, Green diesel synthesis by hydrodeoxygenation of bio-based feedstocks: Strategies for catalyst design

REFERENCES (continues)

and development, Renewable and Sustainable Energy Reviews, 48, 240-255p.

Cibaria International.INC., http://www.cibaria-intl.com/themes/main/spec.php (last accessed January 2017)

Doronin, V., P., Potapenko, O., V., Lipin, P., V., Sorokina, T., P., 2013, Catalytic cracking of vegetable oils and vacuum gas oil, Fuel, 106, 757-765p.

Duman, G., Azhar Uddin, Md., Yanik, J., 2014, Hydrogen production from algal biomass via steam gasification, Bioresource Technology, 166, 24-30p.

Galadima, A., Muraza, O., 2015, Cataltic upgrading of vegetable oils into jet fuels range hydrocarbons using heterogeneous catalysts: A review, journal of industrial and engineering chemistry, 29, 12-23p.

Görez, T. and Alkan, A., 2005, Türkiye'nin yenilenebilir enerji kaynakları ve hidroelektrik enerji potansiyeli, Dokuz Eylül üniversitesi mühendislik fakültesi, inşaat mühendisliği bölümü, 5p.

Huber, G., W., O'Connor, P., Corma, A., 2007, Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures, Applied catalysis A: general, 329, 120-129p.

Irkıçatal Oğuz, B, Yenilenebilir enerji kaynakları, Elektrik piyasası dairesi kurumu, (last accessed December 2016).

Jęczmionek, Ł., Porzycka-Semczuk, K., 2014, Hydrodeoxygenation, decarboxylation and decarbonylation reactions while co-processing vegetable oils over NiMo hydrotreatment catalyst. Part II: Thermal effects - experimental results, Fuel, 128, 296-301p.

Karakaya, E. ve Mercan, M., 2013, Sera gazı salımının azaltımında alternatif politikaların ekonomik maliyetlerinin incelenmesi: Türkiye için genel denge analizi, Erciyes Üniversitesi İktisadi ve İdari Bilimler Fakültesi Dergisi, Sayı: 42, Temmuz-Aralık 2013: 123-159p.

REFERENCES (continues)

Karayılmazlar, S., Saraçoğlu, N., Çabuk, Y. ve Kurt, R., 2011, Biyokütlenin Türkiye'de enerji üretiminde değerlendirilmesi, Bartın Orman Fakültesi Dergisi,13,19: 63-75p.

Kiatkittipong, W., Phimsen, S., Kiatkittipong, K., Wongsakulphasatch, S., Laosiripojana, N., Assabumrungrat, S., 2013, Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil, Fuel Processing Technology, 116, 16-26p.

Kim, S., K., Brand, S., Lee, H., Kim, Y., Kim, J., 2013, Production of renewable diesel by hydrotreatment of soybean oil: Effect of reaction parameters, Chemical Engineering Journal, 228, 114-123p.

Koçar, G., 2014, Biyokütle enerji teknolojileri: Biyokütle tanımı, kullanımı, kaynakları ve karakterizasyonu, EÜ Güneş Enerjisi Enstitüsü, 2014 Kış Okulu.

Lavrenov, A.,V., Bogdanets, E., N., Chumachenko,Yu., A., Likholobov, V., A., 2011, Catalytic processes for the production of hydrocarbon biofuels from oil and fatty raw materials: contemporary approaches, ISSN 2070-0504, Catalysis in Industry, 2011, Vol. 3, No. 3, 250–259p.

Lee, Y., Park, J., Ryu, C., Gang, S., Yang, W., Park, Y., Jung, J. and Hyun, S., 2013, Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 ºC, Bioresource Technology 148 (196): 196-201. and Biochemistry, 43: 1812-1836. enhancement, 257-281p.

Lehmus, P., VP R&D, Neste Oil, 2014, European Biofuels Technology Platform http://www.biofuelstp.eu/spm6/docs/petri-lehmus.pdf (last accessed January 2017)

Myers, M., E., Stollstelmer, J., J., Wims, A., M., 1975, Determination of Hydrocarbon-Type Distribution and Hydrogen/Carbon Ratio of Gasolines by Nuclear Magnetic Resonance Spectrometry, Analytical Chemistry, Vol. 47, No. 12, 2010-2015p.

REFERENCES (continues)

Nigam, P., S., Singh, A., 2010, Production of liquid biofuels from renewable resources, Progress in Energy and Combustion Science, 37, 52-68p.

Nimkarde, M., R., Vaidya, P., D., 2016, Toward diesel production from karanja oil hydrotreating over CoMo and NiMo catalysts, Energy Fuels, 30, 3107-3112p.

Pinto, F., Martins, S., Gonçalves, M., Costa, P., Gulyurtlu, I., Alves, A., Mendes, B., 2013, Hydrogenation of rapeseed oil for production of liquid bio-chemicals, Applied Energy, 102, 272-282p.

Šimáček, P., Kubička, D., 2010, Hydrocracking of petroleum vacuum distillate containing rapeseed oil: Evaluation of diesel fuel, Fuel, 89, 1508-1513p.

Šimáček, P., Kubička, D., Šebor, G., Pospíšil, M., 2010, Fuel properties of hydroprocessed rapeseed oil, Fuel, 89, 611-615p.

Šimáček, P., Kubička, D., Kubičková, I., Homola, F., Pospíšil, M., Chudoba, J., 2011, Premium quality renewable diesel fuel by hydroprocessing of sunflower oil, Fuel, 90, 2473-2479p.

Susanto, B., H., Nasikin, M., Sukirno, Wiyo, A., 2014, Synthesis of renewable diesel through hydrodeoxygenation using Pd/zeolite catalysts, Procedia Chemistry, 9, 139-150p.

Şenpınar, A. and Gençoğlu, M. T. , 2006, Yenilenebilir enerji kaynaklarının çevresel etkileri açısından karşılaştırılması, Doğu Anadolu Bölgesi Araştırmaları, 49-54p.

Topal, M. and Topal Arslan, E. I., 2012, Ürün bitkilerinden yenilenebilir enerji kaynağı biyokütle enerjisi potansiyelinin belirlenmesi, Afyonkarahisar İli Örneği (2006-2010).

Uskan, B., 2009, Odun talaşının hidrotermal dönüşümünden elde edilen kimyasalların karakterizasyonu, Yüksek Lisans Tezi, AÜ Fen Bilimleri Enstitüsü Kimya ABD, 96p.

REFERENCES (continues)

Veriansyah, B., Han, J., Y., Kim, S., K., Hong, S., A., Kim, Y., J., Lim, J., S., Shu, Y., W., Oh, S., G., Kim, J., 2012, Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts, Fuel, 94, 578-585p.

Wannapeera, J., Fungtammasan, B. and Worasuwannarak, N., 2011, Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass, Journal of Analytical and Applied Pyrolysis 92 (99): 99-105p.

Wi, S., G., Kim, H., J., Mahadevan, S., A., Yang, D., J., Bae, H., J., 2009, The potential value of the seaweed Ceylonmoss (Gelidium amansii) as an alternative bioenergy source, Bioresource Technology, 100, 6658-6660p.

Yoon, J., J., 2011 What's the difference between biodiesel and renewable (Green) diesel http://advancedbiofuelsusa.info/wp-content/uploads/2011/03/11-0307-Biodiesel-vs-Renewable_Final-_3_-JJY-formatting-FINAL.pdf (last accessed January 2017)