

**INVESTIGATION OF BIODIESEL PRODUCTION
FROM SAFFLOWER OIL**

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ABSTRACT
MSc Dissertation
INVESTIGATION OF BIODIESEL PRODUCTION
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Waleed O.M.M.AHMED
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Supervisor: Prof. Dr. Hasan Ferdi GERÇEL
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In this study, first of all, the properties of safflower oil, acid value, iodine value, peroxide value, saponification number, kinematic viscosity and density were determined. In the second step, the ester content of safflower oil into biodiesel was investigated through transesterification reaction in the presence of base-catalyzed. Different experimental variables such as oil/ethanol molar ratio (1:3, 1:6 and 1:9), sodium methoxide (NaOCH₃) catalyst concentration (0.25%, 0.50%, 0.75% and 1.00%) were investigated, while the rate of stirring 600 rpm and reaction temperature 65±1°C conditions were kept constant. As a result, oil/ethanol molar ratio of 1:6, catalyst concentration of 1.00%, rate of stirring of 600 rpm, reaction temperature of 65±1°C and 20 min reaction duration offered the best safflower oil ethyl ester yield (99.2 %). Characterization of the fatty acid methyl esters (FAMEs) was accomplished by Iatroscan MK-6s TLC/FID.

Keywords: Energy, Biodiesel, Safflower oil, Transesterification, TLC/FID

ÖZET
Yüksek Lisans Tezi
ASPIR YAĞINDAN BİYODİZEL ELDESİNİN ARAŞTIRILMASI

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Bu çalışmada, öncelikle aspir yağının özellikleri; asit değeri, iyot değeri, peroksit değeri, sabunlaşma sayısı, kinematik viskozitesi ve yoğunluğu belirlenmiştir. Daha sonra aspir yağının bazik-katalizör varlığında transesterifikasyon reaksiyonu ile biyodizelin ester içeriği araştırılmıştır. Yağ/etanol oranı (1:3, 1:6 ve 1:9), sodyum metoksit (NaOCH₃) katalizör konsantrasyonu (%0.25, %0.50, %0.75 ve %1.00) gibi değişkenler incelenmiş ve karıştırma hızı 600 rpm ve reaksiyon sıcaklığı 65±1°C deney koşullarında sabit tutulmuştur. Aspir yağının yağ asidi metil esterlerine veriminin incelenen şartlarda en iyi verim, 1:6 yağ/etanol oranı, % 1.00 sodyum metoksit katalizör konsantrasyonu, 600 rpm karıştırma hızı ile, 65±1°C reaksiyon sıcaklığında ve 20 dakikalık reaksiyon süresinde %99.2 ile gerçekleşmiştir. Yağlı asidi metil esterlerinin karakterizasyonu (FAMEs) Iatroscan MK-6s (TLC/FID) cihazı tayin edilmiştir.

Anahtar Kelimeler: Enerji, Biyodizel, Aspir yağı, transesterifikasyon, TLC/FID.

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ABBREVIATIONS

AOCS	American Oil Chemist Society
ASTM	American Society of Testing and Materials
EN	European Normalization
UNI	Italian National Standards Institute
SS	Swedish Standards Institute
DIN	German Institute for Standardization
ONC	Austrian Standard
FAME	Fatty Acid Methyl Ester
FAEE	Fatty Acid Ethyl Ester
VOME	Vegetable Oil Methyl Ester
SOEE	Safflower Oil Ethyl Ester
SO	Safflower Oil
B100	Hundred Percent Biodiesel
XX	Blend Ratio of Diesel fuel to the Biodiesel
BD	Biodiesel
EE	Ethyl Ester
TG	Triglycerides
FFA	Free Fatty Acids
DG	Diglycerides
MG	Monoglycerides
FA	Fatty Acids
^1H NMR	Proton Nuclear Magnetic Resonance
GC	Gas Chromatography
CFPP	Cold Filter Plugging Point

SO _x	Sulfur Oxides
NO _x	Nitrogen Oxides
CO _x	Carbon Oxides
VOCs	Volatile Organic Compounds
PM	Particulate Matter
MeOH	Methanol
SCM	Supercritical Methanol
%	Percent
AV	Acid Value
IV	Iodine Value
PV	Peroxide Value
SV	Saponification Value
phph	Phenolphthalein
CHL	Chloroform
AA	Acetic Acid
CN	Cetane Number
CP	Cloud Point
PP	Pour Point
TLC	Thin Layer Chromatography
FID	Flame Ionization Detector
RPM	Revolution Per Minute
MT	Metric Ton
THF	Tetrahydrofuran
CSTR	Continuous Stirred-Tank Reactor
PFR	Plug Flow Reactor

1. INTRODUCTION

According to the recent increase in oil consumption, many concerns have risen about the future of fuel which is the major source of energy. The energy demands have been met so far by the use of fossil resources that has been now leading to the depletion of those reserves. Besides the depletion of these reserves, the negative environmental impacts such as global warming, ozone depletion, eutrophication and photochemical smog, acidification and deforestation led to the urgent need for using alternative energy that would be economically efficient, environmentally intact and socially equitable. Based on the fact that fuel demand in a steady increase, these expectations may stay without change until coming decades because of the increased number of vehicles and people at the present time. The demand for fossil fuels in a significant increase in time that the resources began to run out, therefore, it is expected that the price of fossil fuels will increase. As a result, the expected scarcity of fossil fuels and the negative environmental impacts resulting from using fossil fuels have led to research on renewable transportation biofuels (Hill, Nelson, Tilman, Polasky, & Tiffany, 2006).

The serious impacts of using petroleum-derived fuels on the environment has distinctly affected the spread of alternative fuels, which are materials other than petroleum-derived products used to run the engine (Prah, 2010). The petroleum became more expensive in terms of identifying the place and extraction. Moreover, the environmental studies on global warming and emissions of diesel exhaust paved the way for the emergence of biodiesel as a potential alternative for diesel fuel (Knothe, Gerpen, & Krahl, 2005). Other examples for alternative renewable sources of energy are solar thermal and photovoltaic, tidal, biomass (wood, wood waste, plant/crop-based renewables, agricultural wastes, food wastes, and algae), biofuels including bioethanol, bio-hydrogen, and biodiesel (Lee, Speight, & Loyalka, 2007), water, sun, wind and geothermal (Boudghene Stambouli & Traversa, 2002). These sources have been taken into consideration based on expectations that the transport on a global scale will start

to intensification demand for fossil fuel with up to a maximum annual growth of 1.3 % up to 2030 to hit 42340 million barrel per year (116 million bbl/day up from 84 million bbl/day in 2005) (Pickett, 2008).

Efforts have been made to reduce the emissions of air pollutants associated with combustion processes, which include sulfur oxides SO_x, nitrogen oxides NO_x, carbon oxides CO_x, volatile organic compounds VOCs, particulate matter (PM) and others. These efforts have contributed greatly to the promotion of air quality and related technologies (Lee et al., 2007). In fact, finding alternative fuel is not to ensure the sustainability just, but also to be environment friendly.

By comparing with petroleum diesel fuel and biodiesel, it was found that the biodiesel is biodegradable, non-toxic and has a low-emission features (Ma & Hanna, 1999). Biodiesel indicates to the pure or absolute fuel before blending with diesel fuel, and due to the similarity of characteristics between biodiesel and diesel fuel, it can be mixed with each other by certain percentages. The synthesizer knows as "BXX" where "XX" is the blend ratio of diesel fuel to the biodiesel (Sankar, 2014).

1.1. Biodiesel Blend

According to American Society for Testing and Material (ASTM), the definition of biodiesel blend is: “a blend of biodiesel fuel with petroleum based diesel fuel”. Biodiesel blends are predominantly designated with the abbreviation BXX, where XX indicates to the volume (in percent) of biodiesel fuel in the blend ((ASTM), 2010). Accordingly, B2 is constituted by 2% of B100 (Biodiesel), and 98% of diesel (Monteiro, Ambrozin, Lião, & Ferreira, 2008). This ratio has become a mandatory use in Minnesota in most of the state’s diesel fuel supply, but by 2007, the governor of Minnesota announced a plan to promote the increase proportion of biodiesel gradually from B2 to B20 by 2015 as B2, B5, B10, B15 and B20 in 2008, 2011, 2013 and 2015 (Chuanfang, Lee, Larsen, & Madsen, 2008). In september 2011, Turkish Energy Regulatory Agency (EMRA) announced that the biofuel blending will be compulsory by 2013 and 2014 for biodiesel and bioethanol with mixing ratios of 1% and 2% respectively. This ratio

of biodiesel blending reached 2% by 2015 and will be increased to 3% by 2016 (Boluk & Koc, 2013).

There is a very great affinity in the kinematic viscosity of biodiesel and diesel fuel, this deeply elucidates the reason of transesterifying vegetable oils and animal fats to alkyl esters (biodiesel) (Knothe et al., 2005). Lower-viscosity fuel is required for the vast majority of engines to insure more efficient with time, otherwise, the high viscosity of un-transesterified oils and fats could cause harm in diesel engines such as deposits on various parts, thus damage of the engine (Knothe et al., 2005).

The cetane number is the precise index of ignition quality (C. M. Scrimgeour & Harwood, 2007). In fact, diesel fuel has a lower cetane number than biodiesel; it contains 10% to 11% oxygen by weight, no aromatics and almost no sulfur. These characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compared to petroleum-based diesel fuel (Canakci & Gerpen, 2001). The other significant properties are pour point, cloud point, viscosity (C. M. Scrimgeour & Harwood, 2007), heat of combustion, oxidative stability and lubricity which among the most significant one of these properties (Knothe et al., 2005). Table 1.1 below shows a comparison between biodiesel B100, biodiesel blend B20 and diesel fuel in some properties.

Table 1.1. Comparison between Biodiesel B100, Biodiesel Blend B20 and Diesel Fuel in some Properties

Fuel	Biodiesel B 100	Biodiesel B20	Diesel Fuel
Boiling point (760 mmHg) ^B	>200°C ^B	171°C=(340°F) ^C min	~ 150°C (~302°F) ^C
Melting point	~ 4°C	NA ^C	~ -25° C (-13°F)
Flash point (closed cup) ^A	min, 130°C ^A	66°C = (149.7°F) ^C	min 38°C (100°F) ^C
Specific gravity ^B ,H2O=Unity	0.88 ^B	0.879 ^C	0.82 ^C
Vapor pressure, mmHg ^B	< 2 ^B	< 1 ^C	< 2 ^C
Cetane number ^A	min, 47 ^A	-	Min 40
Autoignition temperature	-	610°C (1131.4°F) ^C	>254°C (489.2°F) ^C
Kinematic viscosity at 40°C ^A	1.9 – 6.0 ^A	-	-
Acid number ^A	0.8 ^A	-	-
Density	-	8.18 lbs/gal ^C	~ 6.8 lbs/gal ^C

Source: ^A ((ASTM), 2010), ^B (biodiesel.org, n.d.), ^C (Department, 2007)

The presence of FA in vegetable oils or animal fats indicates that there is a difference in the chemical composition of each type which emerges different in the chemical and physical properties of the biodiesel such as cloud and pour point (Prah, 2010).

According to (C. M. Scrimgeour & Harwood, 2007), “Fatty acids are aliphatic, usually straight chain, monocarboxylic acids”. The FA chain length between C16 and C22, and in most oils found that C18 is the most dominate FA (C. Scrimgeour, 2005). Table 1.2 below shows the FA composition of the most commonly traded commodity oils (C. Scrimgeour, 2005) and (Prah, 2010).

Table 1.2. Component acids of the major oils, wt.%

Oil Source	16:0	18:0	18:1	18:2	18:3	Other
Corn	13	3	31	52	1	-
Cottonseed	27	2	18	51	Trace	2
Groundnut	13	3	38	41	Trace	C20-245
Linseed	6	3	17	14	60	-
Olive	10	2	78	7	1	2
Palm	44	4	40	10	Trace	2
Palm olein	40	4	43	11	Trace	2
Palm stearin	47-69	~5	20-38	4-9	Trace	-
Rape (low erucic)	4	2	56	26	10	20:1 2
Rice bran	16	2	42	37	1	2
Safflower(high linolenic)	7	3	14	75	-	1
Safflower (high oleic)	6	2	74	16	-	2
Sesame	9	6	38	45	1	1
Soybean	11	4	22	53	8	2
Sunflower (high linoleic)	6	5	20	69	Trace	-
Sunflower (high oleic)	4	5	81	8	Trace	2
Tall oil	5	3	46	41	3	2

Source: (Prah, 2010).

1.2. Research Objectives

Because of the increasing concerns about potential of global climate change, declining air purity, water quality and human health concerns nowadays, the idea came to produce the biodiesel from vegetable oil to reduce the negative impact on the surrounding environment that caused by fossil diesel. The investigation about biodiesel production carried out by experiments using the optimal way which gives the best conversion ratio.

In this study safflower oil was chosen to react with ethyl alcohol in the presence of sodium methoxide (NaOCH_3) as a catalyst to produce biodiesel. The product biodiesel was analysed by Iatroscan MK-6s using thin layer chromatography and flame ionization detection (TLC/FID) to find out the highest possible ester content, therefore, our study is completely original.

We conclude that, the main objective is to investigate about the best way to enhance the biodiesel production, then bring it in place of fossil fuels which uses in diesel engines to help prolong engine life and to reduce the negative impact on the surrounding environment over the long term.

2. VEGETABLE OIL BASED DIESEL FUELS

2.1. History

Obtaining of biodiesel from vegetable oils is very old process. The responsible operation for converting vegetable oils or animal fats to biodiesel (mono alkyl esters) known as transesterification which applied in the early of 1853 by scientists E. Duffy and J. Patrick. In 1893 a paper entitled “The theory and construction of a rational heat engine” was published by German inventor Dr. Rudolf Diesel where explained the revolutionary engine which works on compress the air by a piston to obtain a high temperature. He designed his diesel engine to run on vegetable oil (Demirbas, 2009).

Vegetable oils and animal fats were investigated in 1970 as a diesel fuels before energy crises and early of 1980 where it was aroused great interest on alternative fuel (Knothe et al., 2005). The first biodiesel was recommended by Walton in Gas Oil Power journal entitled (The Fuel Possibilities of Vegetable Oils) in 1938 that “To get the utmost value from vegetable oils as fuel it is academically necessary to split off the triglycerides and to run on the residual fatty acid. Practical experiments have not yet been carried out with this; the problems are likely to be much more difficult when using free fatty acids (FFA) than when using the oils straight from the crushing mill. It is obvious that the glycerides have no fuel value and in addition are likely, if anything, to cause an excess of carbon in comparison with gas oil” (D.L. Van Dyne, 1996) and (Knothe et al., 2005). Biodiesel production process is not a complex process where it can be produced from variety of feedstock’s which include multidisciplinary vegetable oils such as safflower, palm, peanut, rapeseed/canola, sunflower, soybean, cottonseed and coconut; animal fats such as tallow which is using usually in addition to using waste oils such as frying oils (Knothe et al., 2005). These enormous varieties of feedstock’s are capable to encourage the scholars to develop and inclusion biodiesel among the important current and future fuel projects.

It's expected that the use of vegetable oil for biodiesel production will increase annually by 2.1% throughout the next ten years. The vegetable oil share that used to obtain biodiesel worldwide is anticipated to stay constant in 2024 at 13% of the world demand of vegetable oil. Figure 2.1 shows the vegetable oil

used for biodiesel production in some countries which are considered the highest in the production, while the remaining production of the other countries around the world mentioned as (world) with countries (OECD/FAO, 2015).

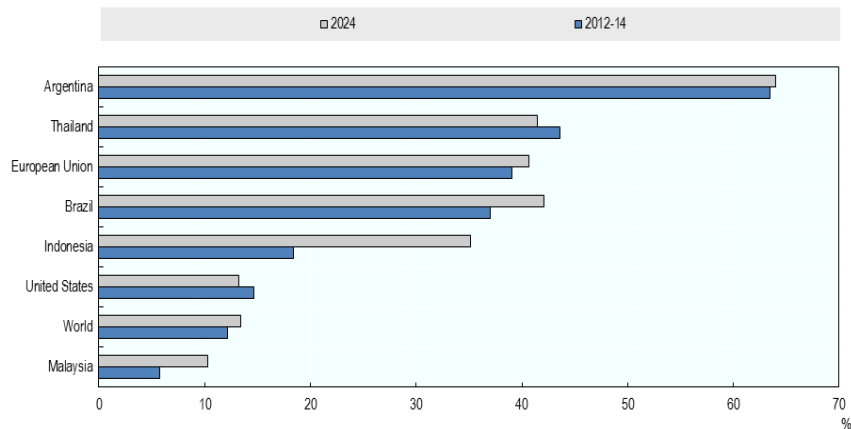


Figure 2.1. Vegetable oil used for biodiesel production (OECD/FAO, 2015)

2.2. Composition of Vegetable Oils

Based on fact that vegetable oils consist 90-98% triglyceride (TG) where make it the essential constituent of vegetable oils with small amounts of monoglycerides (MG) and diglycerides (DG). TG are results from the interaction between three FA with glycerol, and these contain large amounts of oxygen in its structure. There is variation in carbon chain length in FA and double bonds number. Table 2.1 below shows prevalent and widespread FA such as oleic, palmitic, linoleic, linolenic and stearic, and Table 2.2 shows some vegetable oils chemical composition (Srivastava & Prasad, 2000). Generally vegetable oils contain 1-5 % of FFA, phospholipids, carotenes, phosphatides, sulphur compounds, traces of water and tocopherols (Srivastava & Prasad, 2000).

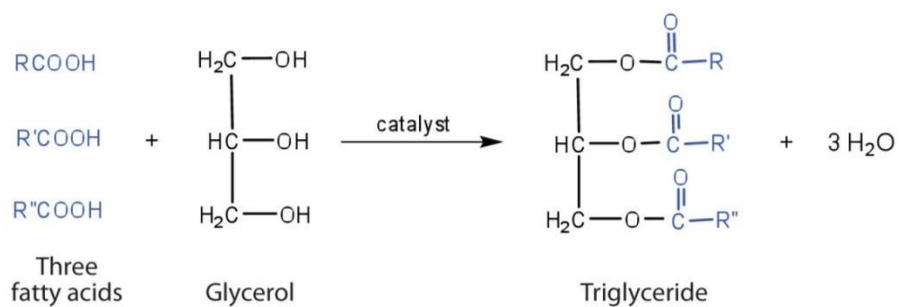


Figure 2.2. (-OH) groups on the glycerol molecule are esterified with the same FA and obtained ester called a simple triglyceride

Table 2.1. Prevalent and Widespread Fatty Acids

Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic	<i>Cis</i> -9-Octadecanoic	18:1	C ₁₈ H ₃₄ O ₂
Linoleic	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic	<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15-Octadecatrienoic	18:3	C ₁₈ H ₃₀ O ₂
Erucic	<i>cis</i> -13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

Source: (Srivastava & Prasad, 2000).

Table 2.2. Some vegetable oils chemical composition

Vegetable oil	Fatty acid composition, wt. %									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr ^a	0	0	25	0	6	Tr ^a
Cottonseed	0	28	1	0	0	0	13	0	58	0
Cramble	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
High oleic Safflower	Tr ^a	5	2	Tr ^a	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0

Source: (Srivastava & Prasad, 2000), Tr^a = Traces.

2.3. Fuel Related Properties of Vegetable Oils

There is variation in the kinematic viscosity of vegetable oils in the range of (30-40) cSt at 38°C. The high viscosity of these oils suggests high molecular mass and chemical composition. Molecular mass range of vegetable oils in the range between (600-900), which is three times or more higher than diesel fuel. In case of volumetric heating, the values of these oils comparing with diesel fuel are in range of (39-40) MJ/kg which is mean it is low than diesel fuel (~45 MJ/ kg), and the presence of chemically restricted oxygen in vegetable oils reduce about 10% of their heating values. The ranges of cetane numbers and iodine value are (32-40) and (0-200) respectively according to unsaturation. The cloud and pour points of diesel fuels are lower than that of vegetable oils (Srivastava & Prasad, 2000). Some of the vegetable oil properties shown in the Table 2.3 below:

Table 2.3. Vegetable oils properties

Vegetable oil	Kinematic viscosity at 38°C mm ² /s	Cetane number	Heating value MJ/kg	Cloud point °C	Pour point °C	Flash point °C	Density kg/l	Carbon residue wt %
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148	0.24
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9044	0.23
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236	0.22
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026	0.24
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144	0.25
H.O. Safflower	41.2	49.1	39.5	-12.2	-20.6	293	0.9021	0.24
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133	0.25
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138	0.27
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161	0.23
Palm	39.6	42.0	-	31.0	-	267	0.9180	-
Babassu	30.3	38.0	-	20.0	-	150	0.9460	-
Tallow	-	-	40.0	-	-	201	-	6.21

Source: (Srivastava & Prasad, 2000).

2.4. Performance of Vegetable Oils as Diesel Fuels

Using vegetable oils as diesel fuel directly in the diesel engines lead to many problems associated with the oil quality and climate conditions. There is clear difference in the injection, atomization and combustion between vegetable oils as diesel fuel and those of hydrocarbon-based diesel fuels (Srivastava & Prasad, 2000). It is an accepted fact that viscosity of vegetable oils has affect effectively on the spray characteristics which in turn lead to inferior fuel atomization, higher Sauter mean diameter -the proportion of the mean volume to the mean surface of the fuel droplets- and lower spray speed than conventional diesel fuel (Esteban, Riba, Baquero, Rius, & Puig, 2012). High viscosity vegetable oils interfere with injection process and resulting in poor fuel atomization. The deposit formation, carbonization of injector tips, degradation and ring sticking and lubricating oil dilution are results of high flash point to a minimum degree than the degree of volatility. The low volatility and high viscosity incentive to cause poor cold engine start up, misfire and ignition delay. The thermal polymerization of vegetable oils and oxidative are reasons for deposition on the injectors forming a film that continue to trap fuel and interfere with combustion, so, according to this various types of oil, the engine must be less or more modified (Srivastava & Prasad, 2000).

2.5. Safflower Oil as Alternative for Biodiesel Production

Safflower oilseed crop (*Carthamus tinctorious*) is a member of the family Compositae or Asteraceae and it's the latinized synonym of the Arabic word (gurtum) which refers to the color of the tincture extracted from safflower flowers. There was a diverse written forms of the safflower known as affore,usfar, asfiore and saffiore where the safflower had been inferred from them. Safflower has been grown in India since time abysmal and currently it's widespreadly known as kardai. Other name is hong hua which is prevalent in China. Originally, the safflower classified of broadleaf crop, so, basicly it's grown to take advantage of its flowers. The dyes of safflower crop have a red and yellow color which is used for clothing and food. Presently, the crop is grown for oil as a primary reason and for birdseed. Safflower is long-lasting and able to resist dryness and hail. The

taproot can prolong 8-10 feet into the surface and allow it to benefit from soil moisture and the nitrogen which is existing inside soil. It has been found that the irrigated lands achieved the optimal yields. The rainfall season is taken into account where is growing in zones <15 inches of growing season rainfall. The ability of the plant taproot to indulges strongly inside for subsoil moisture positively improved the produce of Linoleic and Oleic oils to become clearly alternative to existing crops which are grown peripheral nowadays (Berglund, Riveland, & Bergman, 2010; Gilbert, 2008; Mcnew, Bixley, Hall, & Box, 2001; Singh & Nimbkar, 2006).

There are about 60 countries around the world grow safflower crop. Despite the safflower is considered a secondary crop with < 1 million hectares planted, the production estimated each year is about 500,000 mt. Approximately, India produces the half annual production of safflower oil immediately followed by the United States of America in the second place represented in California state which is the highest state in production (Gilbert, 2008). Figure 2.3 shows the significant safflower producing regions.



Figure 2.3. Significant Safflower Producing Regions (Gilbert, 2008).

The safflower seed harvested area, seed amount, production amount and yield during the years from 2000 to 2013 in the world reported in Table 2.4 below.

Table 2.4. Safflower seed harvested area, seed amount, production amount and yield by years in the world.

Year	Harvested Area (Ha)	Seed (ton)	Production (ton)	Yield (Hg/Ha)
2000	825,809.000	20,682.420	625,183.000	7,570.550
2001	802,142.000	18,401.840	550,480.000	6,862.630
2002	727,757.000	24,961.000	546,125.000	7,504.220
2003	890,089.000	26,082.490	706,601.000	7,938.540
2004	964,647.000	21,093.700	655,704.000	6,797.350
2005	838,686.000	17,740.680	587,041.000	6,999.530
2006	704,703.000	19,989.470	534,928.000	7,590.830
2007	755,054.000	18,141.520	627,249.000	8,307.340
2008	721,961.300	18,623.310	629,348.000	8,717.200
2009	795,096.000	18,375.200	652,926.000	8,211.910
2010	810,450.000	18,868.300	652,773.600	8,054.460
2011	784,407.000	25,426.920	673,026.600	8,580.070
2012	953,332.000	22,022.060	837,310.600	8,782.990
2013	816,588.000	22,147.300	670,318.600	8,208.770

Source: (Production Statistics - Crops, Crops Processed - February 2015 - knoema.com).

URL: <http://knoema.com/FAOPRDSC2015Feb/production-statistics-crops-crops-processed-february-2015>

Turkish Statistical Institute (TÜİK) announced that the production of safflower seed increased by 17,000 ton from 2013 and reached 62,000 ton in 2014. Table 2.5 below shows the safflower seed cultivation area, harvested area, production amount and yield during the years from 2010 to 2014 in Turkey.

Table 2.5. Safflower seed cultivation area, harvested area, production amount and yield by years in Turkey.

Year	Cultivated Area (decare)	Harvested Area	Production (ton)	Yield (kg/da)
2010	135,000	134,978	26,000	193
2011	131,668	131,644	18,228	138
2012	155,918	155,898	19,945	128
2013	292,920	292,599	45,000	154
2014	443,050	439,350	62,000	141

Source: (Ministry of Food, Agriculture and Livestock, Turkey & TÜİK, 2015).

URL: <http://rapory.tuik.gov.tr/20-11-2015-10:49:46-6293197045847664261937577075.html>

The high linoleic acid in safflower believed to lower the ratio of cholesterol and decrease heart disease beside their various usages in

manufacturing paints and surface coatings. After the process of oil extracting, the high protein fodder convenient to use for livestock consumption. Moreover, safflower oil uses dramatically nowadays to obtain biodiesel as an alternative for fossil fuel (Mcnew et al., 2001). The FA which were widespreadly found in safflower oil were myristic (14:0), palmitic (16:0), Margaric (17:0), stearic (18:0), oleic (18:1), linoleic (18:2), arachidic (20:0), gadoleic (20:1), behenic (22:0), and lignoceric (24:0). According to (Sagioglu, Selen, Ozcan, Paluzar, & Toprakkiran, 2011), safflower oil contain a high percentage of linoleic acid (72.3%) as shown in Table 2.6.

Table 2.6. Fatty acid composition of safflower oil

Fatty acid	Systematic name	Formula	Structure	Wt.%
Myristic acid	Tetradecanoic	$C_{14}H_{28}O_2$	14:0	0.30
Palmitic acid	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	7.3
Margaric acid	Heptadecanoic	$C_{17}H_{34}O_2$	17:0	0.03
Stearic acid	Octadecanoic	$C_{18}H_{36}O_2$	18:0	1.9
Oleic acid	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	13.6
Linoleic acid	cis-9,cis-12 Octadecedianoic	$C_{18}H_{32}O_2$	18:2	72.3
Arachidic acid	Eicosanoic	$C_{20}H_{40}O_2$	20:0	0.3
Gadoleic acid	Cis-9-Eicosenoic	$C_{20}H_{38}O_2$	20:1	0.19
Behenic acid	Docosanoic	$C_{22}H_{44}O_2$	22:0	0.28
Lignoceric acid	Tetracosanoic	$C_{24}H_{48}O_2$	24:0	0.01

Source: (Sagioglu et al., 2011); (Karabaş, 2013).

2.6. The Derivatives of Triglycerides as Diesel Fuels

There are four techniques applied to solve the problems faced with the high fuel viscosity which are dilution, microemulsification, pyrolysis and transesterification. Among these transesterification which is the most prevalent way to reduce the viscosity of vegetable oil in biodiesel production (Demirbas, 2009).

2.7. Transesterification

Transesterification, also called alcoholysis is a reaction of oil or fat TG with an alcohol in the presence of catalyst such as sodium hydroxide to form esters and glycerol. Figure 2.4 below shows the TG transesterification reaction (Demirbas, 2009) where the FA chains R' , R'' and R''' are long hydrocarbons

chains (Gerpen, Peterson, & Goering, 2007) . Usually, the catalyst used to improvement the reaction rate and yield. Since transesterification reaction is reverse reaction, excess alcohol is used to displace equilibrium toward products (Demirbas, 2009).

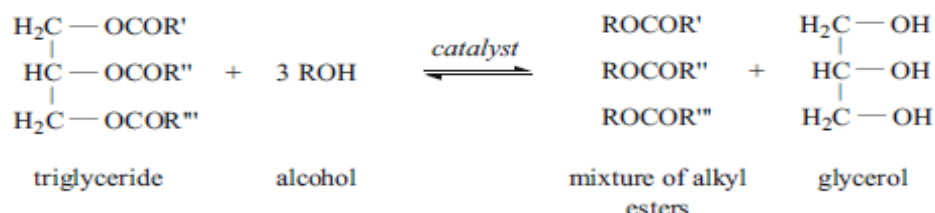


Figure 2.4. Transesterification of Triglycerides with Alcohol (Demirbas, 2009).

2.8. Chemistry of Transesterification Process

Vegetable oils and animal fats have uncommonly comparable chemical structures, even though they may have difference in color and flavor. Transesterification reduce the molar mass of vegetable oils or fats to one third compared to the TG (Chi, 1999). Figure 2.5 shows the overall transesterification reaction, however three reversible and consequence reactions as shown below are believed to happen:

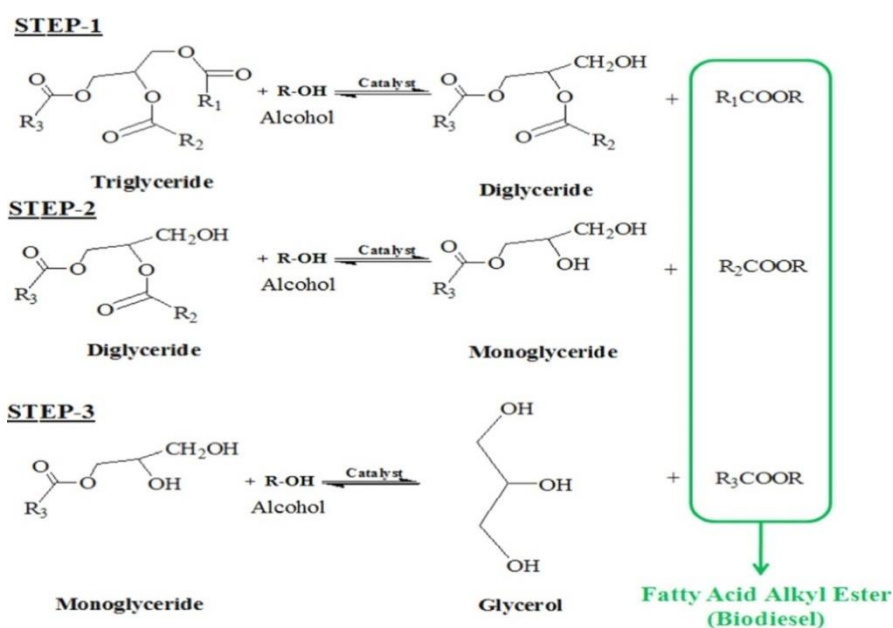


Figure 2.5. Transesterification of Vegetable Oils Chemistry (Avhad & Marchetti, 2015).

These equations elucidate the formation of ester in each step by conversion of TG to DGs followed by DGs to MGs conversion and MGs to glycerol (Srivastava & Prasad, 2000), however, the type of catalyst may be base, acid (Chi, 1999) or enzymes (Demirbas, 2009) depending on vegetable oils or fats properties.

2.8.1. Acid-catalyzed transesterification

One of the ways that stimulate transesterification reaction is adding acids. Hydrochloric, phosphoric, sulfuric and organic sulfonic acids are acids which used for transesterification reaction (Fukuda, Kondo, & Noda, 2001) and it is found that they give enormous yields of alkyl esters (Schuchardt, Sercheli, & Matheus, 1998). In spite of the fact which indicates that the acid-catalyst transesterification is slower than based-catalyst transesterification, but, the acid-catalyst transesterification is more convenient for glycerides which have comparatively high FFA contents and more water (Fukuda et al., 2001). For more illustration, (Schuchardt et al., 1998) mentioned that in the existence of 1% mol H_2SO_4 with an oil/alcohol molar ratio of 1:30 at 65 °C for methanolysis of soybean oil lasts 50 hr to complement the vegetable oil conversion above 99%, while the ethanolysis at 78 °C and butanolyses at 117 °C with the same quantities of H_2SO_4 and alcohol take 18 and 3 hr respectively. Figure 2.6 below show the mechanism of the acid-catalyzed transesterification of vegetable oils (Schuchardt et al., 1998).

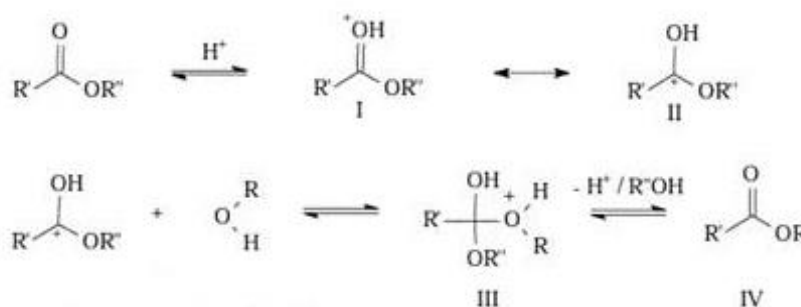


Figure 2.6. Mechanism of Acid-Catalyzed Transesterification of Vegetable Oils which $R'' =$ Glyceride, $R' =$ Carbon Chane of the Fatty Acid, $R =$ Alkyl Group of the Alcohol (Schuchardt et al., 1998).

2.8.2. Alkali-catalyzed transesterification

The alkalis which use for transesterification include sodium hydroxide (NaOH), potassium hydroxide (KOH), carbonates and alkoxides such as sodium methoxide (CH₃ONa), sodium ethoxide (CH₃CH₂ONa), sodium propoxide (CH₃(CH₂)₂ONa), sodium butoxide (CH₃(CH₂)₃ONa), potassium methoxide (CH₃OK), potassium ethoxide (CH₃CH₂OK), potassium propoxide (CH₃(CH₂)₂OK), potassium butoxide (CH₃(CH₂)₃OK) etc. The alkali-catalyzed transesterification in comparison with acid-catalyzed transesterification 4000 times quicker than that catalyzed by the same amount of the acid-catalyzed transesterification, therefore it is commercially used extensively (Fukuda et al., 2001). Figure 2.7 below shows the mechanism of base-catalyst transesterification of vegetable oil.

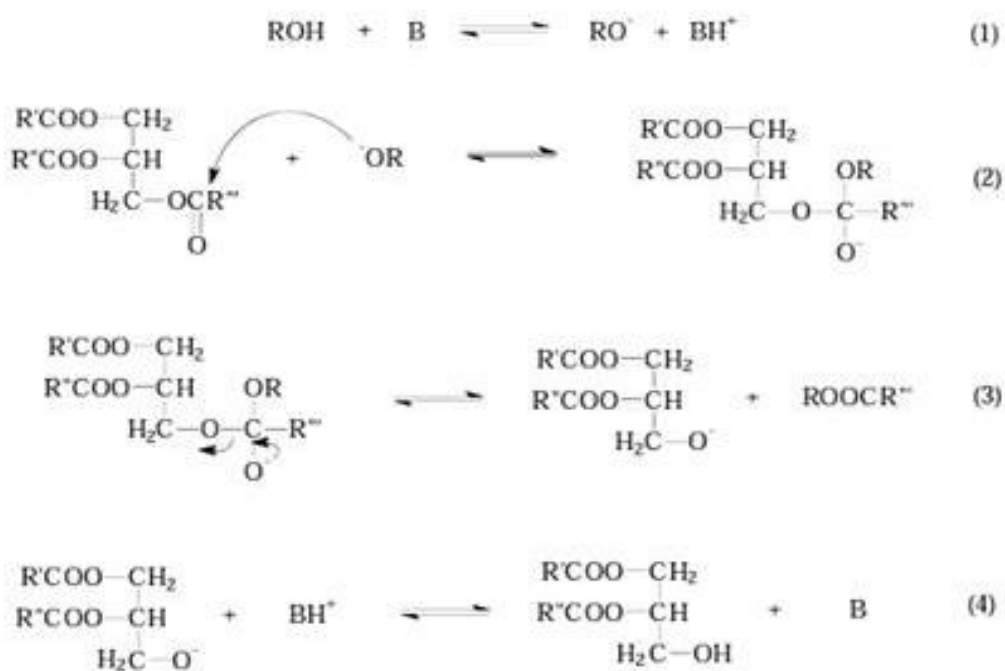


Figure 2.7. Mechanism of base-catalyzed transesterification of vegetable oils (Schuchardt et al., 1998).

On the other hand, there are many factors affecting the process of transesterification where can explain as:

2.8.2.1. Effects of moisture and FFA

The presence of water in transesterification reaction causes partial reactions lead to saponification which produces soap therefore; the reactant (glycerides and alcohol) must be anhydrous to the extent possible. Formation of the soap starts consuming the catalyst and decreases the efficiency as well as leads to increase in viscosity caused by gel formation which in turn makes the investigation of glycerol separation recondite. The FFA of refined oil proposed to be as low as possible, below 0.5%. Esters yields considerably reduced if the reaction running in the absence of catalyst such as NaOH and NaOCH₃, and their reaction with moisture and carbon dioxide lowering their effectiveness (Fukuda et al., 2001).

2.8.2.2. Effects of molar ratio

According to Figure 2.4 which previously mentioned, it is clearly that the stoichiometry of transesterification reaction needs three moles of alcohol for every mole of TG to yield three moles of alkyl ester and one mole of glyceride. Experiments shown that the yield of alkyl ester will be greater in short time if the taken moles of alcohol above three moles (Fukuda et al., 2001). Because the irreversibility of the transesterification reaction, the excess alcohol shift the equilibrium towards products which increases significantly in the biodiesel yield (Ilgen, 2011). For example, Isler et al. (2010) studied the effect of molar ratios 1:3 and 1:6 on ester conversion with raw fleshing oil and they achieved a high conversion with 1:6 molar ratio (Işler, Sundu, Tüter, & Karaosmanoğlu, 2010). Tahvildari et al. (2013) transesterified safflower oil with methanol by taking molar ratios (1:6, 1:7 and 1:8) in the presence of KOH as catalyst (1% w/w) and the results showed that the conversion rising by 2.8% as a result of rising in molar ratio (Tahvildari, Esmaeili, Abdollah, & Sharif, 2013). As general, the molar ratio (1:6) using industrially to obtain methyl ester yields > 98% (Fukuda et al., 2001).

2.8.2.3. Effects of catalyst type

According to (Caldin & Long, 1954), the dissolving of hydroxides in methanol or ethanol lead to formation methoxide and ethoxide. Rashid *et al.*

(2008) investigate the biodiesel production from safflower oil by taking NaOH, KOH, NaOCH₃ and KOCH₃ as catalysts with methanol. The maximum ester conversion was 98% using NaOCH₃ as optimum catalyst (Rashid & Anwar, 2008). The usage of NaOCH₃ has been found more efficient than NaOH, but also sodium and KOH able to catalyst transesterification (Sharma, Singh, & Korstad, 2010). Nevertheless, they are used excessively in the production of biodiesel industrially because of their cheapness (Fukuda et al., 2001).

2.8.3. Enzymatic transesterification by lipase

In spite of advantage of base-catalyzed transesterification for obtaining high conversion of TG to their corresponding alkyl esters in short time of reaction, the reaction have many negatives such as the difficulty in glycerol restoration, intensive of energy, removing acidic or alkaline catalysts from the products, treatment of waste water from alkaline and the water-FFA overlap with the reaction (Fukuda et al., 2001). There are two types of enzymatic biocatalyst, the first one is "extracellular lipases" which the enzyme has already been recovered from the live-producing microorganism gravy and then purgation, while the second one is "intracellular lipases" remains either inside the cell or in the walls which are producing by cell (Gog, Roman, Toşa, Paizs, & Irimie, 2012).

In enzymatic transesterification, it is easier to recover glycerol and by products without any complexity in process, also the FFA in fats and waste oils can be entirely converted to alkyl esters. In short, the production cost of lipase catalyst is significantly higher than that of a base one (Fukuda et al., 2001).

2.8.4. Supercritical transesterification

The substance generally exists in a solid, liquid or gaseous state relying on the pressure and temperature. For example, methanol can changes to a gaseous state when the temperature exceeds the boiling point. On the other hand, when pressure is applied higher than the boiling point, the gaseous substances can be re-compressed again to a liquid state. Gaseous substances cannot be compressed to liquid state after reaching to the critical temperature and vice versa, that's mean

when the compressed liquid reach to the critical pressure, the substance cannot be heat to the gaseous state. Also the substance becomes non-condensable dense fluid when turn into the supercritical fluid higher than inherent critical pressure and temperature. The density in the supercritical state ordinarily falls in a range between 20 to 50 % of that in the liquid state and it's close to that in the gaseous state. To illustrate more, the molecules in the supercritical fluid have high density like a liquid and high kinetic energy like a gas which in turn enhance the chemical reactivity in this state (M. Stoytcheva, 2011).

(Fukuda et al., 2001) discussed the production of biodiesel with supercritical methanol and they confirmed that preheating to 350°C and treatment for 240s in supercritical methanol are enough to convert rapeseed oil to methyl esters. Furthermore, the yield of methyl esters using supercritical methanol method was higher than those obtained by ordinary method with a basic catalyst. The kinetic analysis of the reactions in supercritical methanol and subcritical revealed that the conversion rate of rapeseed oil increase significantly in the supercritical state. Under the parameters of (1:42) rapeseed oil to methanol molar ratio, 45 MPa pressure and 350°C reaction temperature recorded as the best conditions for obtaining a high conversion rapeseed oil methyl ester using supercritical methanol method.

2.8.5. Inorganic heterogeneous catalyst transesterification

Comparatively, the heterogeneous catalysts are permissive to water content and high FFA. It is possible to decrease the total production cost of biodiesel production by development of effective and minimum cost heterogeneous catalysts for transesterification of low cost vegetable oils. Heterogeneous catalysts classified into acidic, basic and biological (enzymatic) types, and the usage of a catalyst from these types rely on feedstock type, cost and availability, operating conditions and required catalyst efficiency. The solid acids prefer esterification and transesterification reactions together for biodiesel with high FFA such as non-edible oils, however, inorganic heterogeneous catalyst fundamentally used because of its availability and cheapness, stability in high temperature and pressure. Furthermore, ease to reactivation and have sturdiness. On other hand,

inorganic heterogeneous catalysts is cost-efficient and have suitable production process as an eco-friendly method, but also have drawbacks where it is need to cruel reaction conditions (pressure and temperature) in some situations and high temperature to modify and prepare active phases (Endalew, Kiros, & Zanzi, 2011).

There are a lot of alkali based metal oxide catalysts such as calcium oxide (CaO), magnesium oxide (MgO), strontium oxide (SrO), hydrotalcites, mixed metal oxides, anionic resins...etc have been tested for transesterification reaction. Among these, CaO is significantly used as heterogeneous catalyst to catalyze transesterification reaction because it have a high basicity and little solubility beside it is cheap and can be handled easily (Avhad & Marchetti, 2015). Many papers have been published on CaO catalyzed transesterification (Ilgen, 2011). (Suryaputra, Winata, Indraswati, & Ismadji, 2013) calcined the waste capiz shells at 900 °C for 2 hr to produce CaO, and then it was used to transesterify palm oil with methanol. It has been noted that using 3 wt% catalyst amounts achieved highest biodiesel yield 92.83% after 6 hr of methanolysis process by applying 1:8 oil/methanol molar ratio at 60 °C. (Correia et al., 2014) obtained CaO catalyst from egg and crab shells to catalyze transesterification reaction between sunflower oil and methanol. It was mentioned that the CaO derived from egg shells have a high basicity, therefore, it was reported that using 1:9 oil/methanol molar ratio, 3 wt% catalyst amount, 60 °C reaction temperature for 3 hr reaction duration achieved 94.10% biodiesel yield.

2.9. Parameters which Influence the Process of Transesterification

The most significant parameters affecting the formation of alkyl esters are:

- Reaction temperature;
- Pressure;
- Molar ratio of alcohol to oil;
- Catalyst type and concentration;
- Mixing intensity;
- Purity of reactants;

- Water content;
- Presence of FFA;
- Reaction time and;
- Degree of refinement of vegetable oil.

Source: (Demirbas, 2009), (Srivastava & Prasad, 2000) & (Knothe et al., 2005).

Among these reaction temperature as an example where we mentioned that at the supercritical state of alcohol, the reaction still low in rate but progressively rise when the temperature or pressure increases. The increase in the temperature specifically in supercritical conditions has affirmative impact on the ester conversion yield, as well, the increase in molar ratio of oil to alcohol leads to increasing in the yield of alkyl ester (Demirbas, 2009).

2.9.1. Mixing intensity

According to transesterification reaction, the reactants initially consist from two-phase liquid system, and the reaction is diffusion-controlled and poor diffusion between the phases results in a slow motion rate. As alkyl esters are formed, their performance as a combined solvent for the reactants and a single-phase system is created. During the slow rate zone of the reaction, the mixing influence is most important, conversely, when the single phase established the mixing becomes insignificant. Understanding of the mixing influence on kinetics of transesterification process is beneficial tool in the design and process scale up (Srivastava & Prasad, 2000).

2.9.2. Purity of reactants

Numerous of experiences confirmed that the ratio of conversion into esters using crude vegetable oils fall between 67 to 84% compared with 94 to 97% when using refined oils which indicate that the impurities existing in the oil affecting in conversion levels. The FFA in the original oils overlap with catalyst, but, under conditions of high pressure and temperature it's possible to overcome these problems (Srivastava & Prasad, 2000).

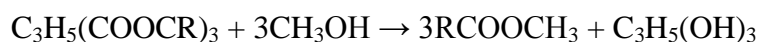
2.9.3. Water content

Water content is a significant factor in the traditional catalytic transesterification of vegetable oil. In the traditional catalytic transesterification of vegetable oils and fats for biodiesel production, the water and FFA produce negative impacts since the existence of them raises the soap formation, depletes the catalyst and diminish efficiency of the catalyst (Demirbas, 2009). Imperatively, the presence of water in the catalyst methods affects negatively on the alkyl esters yields, whereas in the supercritical alcohol method; the presence of water has a favorable impact in alkyl esters formation (Demirbas, 2008).

3. BIODIESEL

3.1. Existent Biodiesel Production Technologies

Essentially, transesterification is a consecutive reaction where the TG firstly converted to DG followed by converting the DG to MG and finally, the MG are converting to the FA esters with reminds that the order of reactions vary with reaction conditions. Nowadays, the biodiesel widely defines as a transesterifying of TG with methanol in the presence of catalyst, and there is conceive that methanol is a preferable alcohol to obtain biodiesel because it is inexpensive to a large extent. The base catalysts are more influence than acid catalysts and enzymes (Demirbas, 2009). Synthetic methanol reacts with TG to obtain methyl esters (biodiesel) and glycerol as shown below:



Triglyceride Methanol Methyl ester Glycerin

There are four essential trajectories to produce biodiesel from oils and fats:

- Base-catalyst transesterification.
- Direct acid-catalyst transesterification.
- Conversion the oil or fat into their FA and then into biodiesel.
- Non-catalytic transesterification.

It's known that the biodiesel which produced by transesterification reactions can be alkali, acid or enzyme catalyzed, however, alkali and acid catalyzed received more attentiveness because the short reaction time, beside low cost compared with enzyme catalyst. Today, the majority of biodiesel production is made with base catalyzed reaction for diversified causes listed as follows:

- Includes low temperature and pressure.
- Yields high conversion (>98%) with insignificant side reactions and reaction time.
- Allows a direct conversion into biodiesel with no intermediate compounds.
- Necessitates simple structure materials.

Figure 3.1 below shows a block diagram of base-catalyzed biodiesel processing that occurs using the following steps of alcohol and catalyst mixing, transesterification reaction, separation, washing of biodiesel, alcohol removal, glycerin neutralization and product quality.

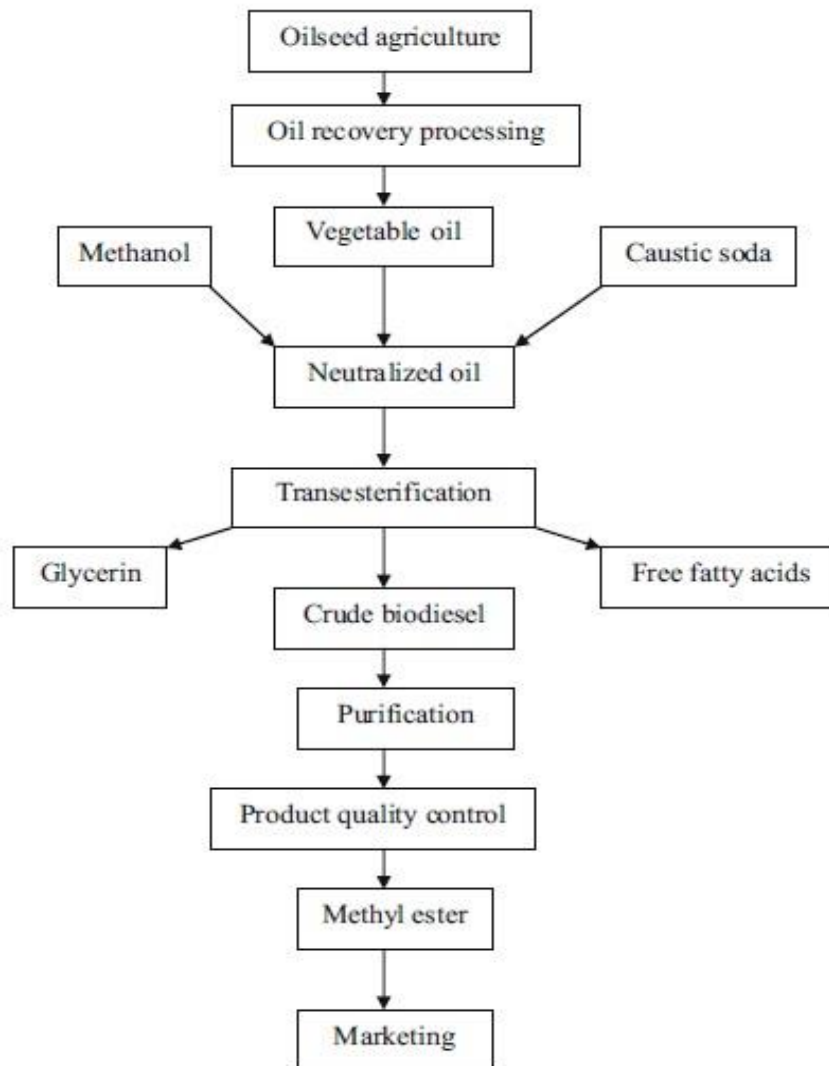


Figure 3.1. Simplified block diagram of base catalyzed biodiesel processing (Demirbas, 2008).

Generally, the basic catalyst is NaOH (caustic soda) or KOH (caustic potash). Practically, caustic soda - or caustic potash - dissolved in the alcohol using mixer or standard agitator and then, the mixture will pass to the reactor to begin interacting with the oil or fat which was already briefly heated in the reactor. The reaction mix is retained solely above the boiling point of methanol

(~344k) to accelerate the reaction and to achieve the transesterification reaction in a short time. The excess of alcohol is commonly used to ensure total conversion of the oil or fat to their alkyl esters. A two main products form in accordance with completion of reaction: biodiesel and tri-alcohol which broadly known as glycerol. The glycerol phase is more intense compared with biodiesel which makes the process of separating by gravity entirely easy. In some operations, a centrifuge uses for separating materials quicker. Biodiesel sometimes purified by washing in a soft way with warm water to expel soaps or residual catalyst then send to storage after drying. The presence of water in alcohols and TG cause soap formation by saponification process, therefore, in alkali-catalyzed transesterification, the TG and alcohols must be anhydrous to a large extent (Demirbas, 2008).

The FFA reacts with alkali catalyst to form soap knowing that fats and oils contain minimal amount of water which leads to soap formation significantly. Since the essential goal is product a high conversion alkyl ester from oil, the soap formation reduces the productivity and makes the separation between ester and glycerol difficult. Alkali-catalyzed transesterification require low FFA content in TG, otherwise the acid catalyzed transesterification should be applied as first step to reduce the FFA content (Demirbas, 2009);(Lu et al., 2009).

In some processes, the biodiesel distilled in a supplementary step to evict the little amounts of color bodies and obtain a colorless biodiesel. After separation process, the overabundant alcohol in each phase expels using a distillation or flash evaporation process. The glycerol as a byproduct includes soaps and non-used catalyst that firstly neutralizing with sulfuric acid then it will sent to the storage as a crude glycerol. Through expulsion the alcohol and water, above than 90% pure glycerol can be produced and it will be ready to be sold in markets. The finished biodiesel must be analyzed using progressing and developed analytical equipment to ensure that it meets ASTM specifications before using as a commercial fuel (Demirbas, 2008).

Table 3.1. Exemplary Proportions for Chemicals Used to Produce Biodiesel (Demirbas, 2008)

Reactants	Amount (kg)
Oil or fat	100.00
Essential alcohol (MeOH)	10.00
Catalyst (NaOH)	0.30
Neutralizer (H ₂ SO ₄)	0.36

The essential raw materials utilized in the biodiesel production are vegetable oils, animal fats and recycled greases, and these materials contain FFA, TG and many different impurities. The other essential raw material to obtain ester is primary alcohol. The catalyst uses in most processes to start the esterification reaction. Also catalyst is desired because the alcohol is moderately soluble in the oil phase. The catalyst enhances the solubility increment to supplement the reaction with a sensible rate. The base catalyst must be neutralized with a strong mineral acid after reaction. Table 3.1 shows the exemplary proportions for chemicals used to produce biodiesel (Demirbas, 2008).

The most significant five parts of biodiesel production to guarantee hassle-free operation in diesel engines are:

- Complete transesterification reaction.
- Elimination of glycerol.
- Elimination of alcohol.
- Elimination of FFA.
- Elimination of catalyst.

3.2. Processes of Biodiesel Production

The molar ratio of glycerides to alcohol, temperature of the reaction, time of reaction, water content and FFA in the oil and the catalyst concentration are the fundamental factors influencing on transesterification reaction. One of the significant aspects in the decision-making process is selecting oils or fats to producing biodiesel. The cost of biodiesel is affected by 70-80% compared to the cost of oils and fats. The crude vegetable oils contain phospholipids and FFA. The phospholipids and FFA are removed in degumming and refining steps

respectively. The excess of FFA can be eliminated as soaps in caustic denudation step or in a later transesterification (Demirbas, 2008).

From the standpoint of chemical reaction, the superior starting material to produce biodiesel is refined vegetable oil because the conversion of perspicuous TG into fatty acid methyl ester (FAME) is high, and the reaction time comparatively short. Despite this, the waste cooking oil would be discharged and cause pollution in the environment, but it can be collecting for additional refinement and then biodiesel processing. This material is a good commercial option to produce biodiesel with low costs (Demirbas, 2008).

Methanol one of the most widespread primary alcohols used in biodiesel production although the other alcohols such as ethanol, isopropanol and butyl can be applied. Water content is the main quality factor of primary alcohol. The interfere between water and transesterification reaction can give a poor yield outcome and high levels of FFAs, soap and TG in the final biodiesel (Demirbas, 2009).

3.2.1. Biodiesel production with batch processing

The resilience of batch process authorizes operating the reactor with various feedstock's and specifications of product (Benavides & Diwekar, 2012). Batch stirred tank reactor is the simplest system for producing alcohol esters. The ratios of TG to alcohol from 1:4 to 1:20 (mole: mole) have been recorded with referring a 1:6 ratio being most widespread. The reactor may be blocked from the top of the tight slot in a head of reactor or equipped with a condenser to reflux alcohol. The operating temperatures from 298 to 358 K have been recorded, but usually about 340 K. NaOH and KOH are most ordinarily applied catalysts under the range from 0.3 to 1.5%. The completion of transesterification reaction has been reported under conversion of 85 to 95%. The higher oil: alcohol ratios and higher temperatures can promote the percent completion too. Reaction times range from 20min to more than 1hr. Firstly, the oil appended to reactor, followed by the catalyst and alcohol mixture. The agitator starting the stirring immediately and it remains to this case during the reaction time, then agitation will stopped. In some

cases, the reaction mixture is leaved to settle in the batch reactor to grant an initial separation of the glycerol and esters. In other cases, the separation of glycerol from alcohol occurring by pumping the mixture into a settling vessel or is separated using a centrifuge process (Demirbas, 2009).

3.2.2. Biodiesel production with continuous processing

In the large plants, using continuous flow processes is very convenient because it reduce cost and time which increases in production and profit (Peterson, Cook, Thompson, & Taberski, 2002). The most widely used reactors are continuous stirred-tank reactors (CSTR) and plug flow reactors (PFR) to produce more than 4 million L/year (Knothe et al., 2005). The commencement of transesterification reaction requirements a strong mixing, and there are various processes that applied strong mixing either from motionless mixers or pumps (Demirbas, 2008). For CSTR, the reaction is achieved in two steps where initially 80% of catalyst and alcohol added to mix with oil, then, the product from this reactor passes through a glycerol removal before entering to the second CSTR. The remaining ratio of catalyst and alcohol (20%) has been added in the second CSTR to give complete reaction using less amounts of alcohol (Knothe et al., 2005). For PFR, The reactor designed in tubular form in lieu of permitting time for the reaction in an agitated tank reactor, and the reaction mixture moves through tubes in a continuous plug. There is a low mixing applied in the axial direction and the result obtained in short times as low as 6 to 10 min for close to consummation of the reaction (Demirbas, 2008).

3.2.3. Biodiesel production with non-catalyzed transesterification

Non-catalyzed transesterification processes divides to supercritical methanol process and BIOX co-solvent process.

3.2.3.1. Supercritical methanol (SCM) process

The minimum value of dielectric constant of MeOH in the supercritical state encourage forming a single phase which is a solution for problems related

with the two phase nature of ordinary MeOH/oil mixture and It has been found that the reaction accomplished in a very short time.

The supercritical methanol process is non-catalytic, include much simpler purification of all products, lower reaction time and more environmentally friendly. The temperature applied in the reaction ranging from 525 to 675 K and the applied pressure range between 35 and 60 MPa. Supercritical transesterification occurs in a high pressure reactor as named as -autoclave- which fills with a certain amount of vegetable oil and liquid methanol taking into account the variance in the molar ratios. An external heater provided the autoclave by heat, and the power set to achieve approximate heating time of 15 min which gauged with iron-constantan thermocouple and monitoring in ± 5 K for a half hour. Transesterification happened during the heating duration, and after each operate, the gas is vented and contains of autoclave sending to received vessel as named as (collector). The remaining contents are washed by methanol to remove it from the autoclave. Figure 3.2 below shows the supercritical transesterification process (Demirbas, 2008).

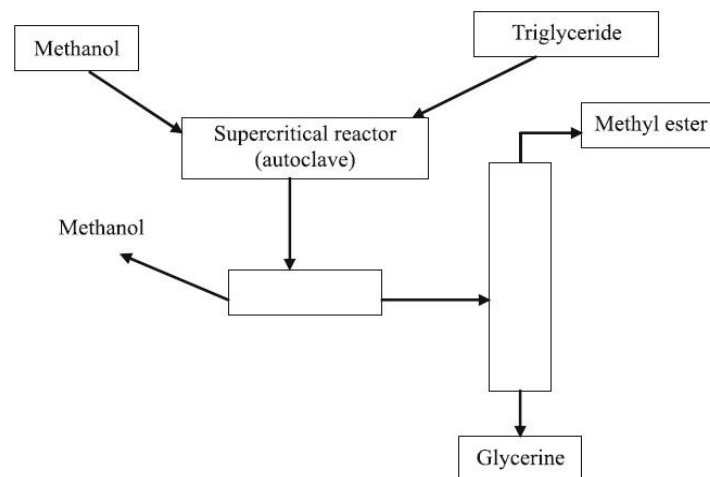


Figure 3.2. Supercritical Transesterification Process (Demirbas, 2008).

3.2.3.2. BIOX process

The exclusive feature of BIOX process is that it uses inert reclaimable cosolvents in a single pass reaction taking a few seconds at ambient pressure and

temperature, so, the objective is to produce biodiesel have ability to rival petrodiesel in cost. Beside the grain based feedstocks, BIOX process also handles animal fats and cooking greases (Demirbas, 2008).

Tetrahydrofuran (THF) as cosolvent specifically uses in the BIOX process to solubilize the methanol. The cosolvent options are designed to overcome slow reaction times resulting from the extremely low alcohol solubility in the TG phase. The result is speedy reaction on the order of 5 to 10 min beside the absence of catalyst remains in either the glycerol or the ester phase. Figure 3.3 below shows the BIOX cosolvent process (Demirbas, 2008).

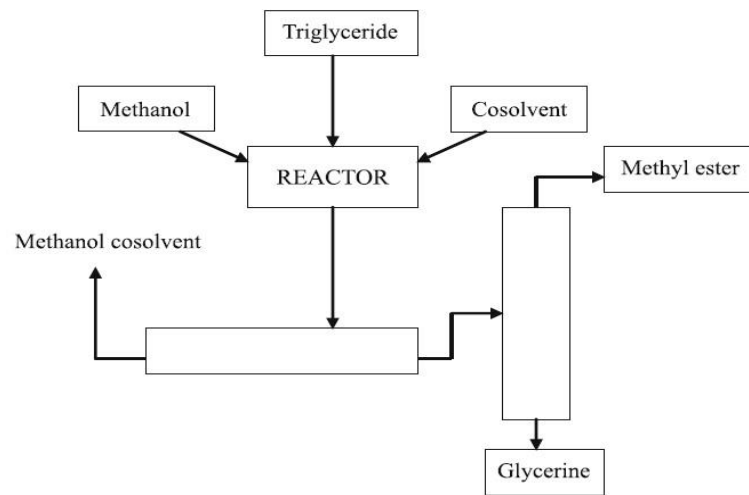


Figure 3.3. BIOX Cosolvent Process (Demirbas, 2008).

(Çağlar, 2007) mentioned that the essential problem of transesterification reaction that the reactants are not easily miscible, thereby increasing reaction time and costs. He transesterified colza oil by reacting with methanol in the presence of KOH as catalyst and THF as cosolvent. 99.89 % conversion was accomplished in very short time (10 min). Also (Mohammed, Ahmad, Hamza, Muazu, & Aliyu, 2012) used THF as effective cosolvent in transesterification of jatropha curcas oil. A highest FAME yield 98% obtained under conditions of 1:4 oil/methanol molar ratio, 1:1 cosolvent/methanol volume ratio, 0.5 w/w NaOH concentration, 40°C reaction temperature, 200 rpm rate of stirring and 10 min reaction duration.

3.3. Biodiesel Standards

Currently, there are two main standards in use; the American Standard for Testing Materials (ASTM) and the European (EN) standards. In spite of the fact that these standards has a lot in common, still there are some parameters that they do not coincide on (Prah, 2010). In various parts of the world, engine manufacturers use slightly diverse standards for biodiesel. Practically, all modern diesel engines correspond with specific specifications to using biodiesel fuel (“Biofuel Systems Group LTD/Biodiesel Standards,” 2013). Each country has specific standards of biodiesel. Table 3.2 below shows the biodiesel standards of some countries:

Table 3.2. Biodiesel standards in various countries

Features	EU	Austria	France	Germany	Italy	Sweden	USA
Standard	TS EN 14214	ONC 1191	Journal Official	DIN V 51606	UNI 10635	SS 155436	ASTM D-6751
Date	2003	July 1997	Septem- ber 1997	Septem- ber 1997	Novem- ber 1996	Novem- ber 1996	January 2002
Application	FAME	FAME	VOME	FAME	VOME	VOME	FAM-AE
Density, 15 °C, g/cm ³	0,86-0,90	0,85- 0,89	0,87- 0,90	0,875- 0,90	0,86- 0,90	0,87-0,90	-
Kinematic Viscosity, 40 °C, mm ² /s	3,5-5	3,5-5	3,5-5	3,5-5	3,5-5	3,5-5	1,9-6
Cold Filter Plugging Point (CFPP), °C	Territorial Property	0/-15	-	0/-10/-20	-	-5	-
Pour Point, °C	-	-	≤-10	-	≤0≤-15	-	-
Copper Corrosion, 3h, 50 °C	1	-	-	1	-	-	≤No,3
Cetane Number	≥51	≥49	≥49	≥49	-	≥48	≥47
Neutralization Number, mg KOH/g	≤0,5	≤0,8	≤0,5	≤0,5	≤0,5	≤0,6	≤0,8
Alkalinity, mg/kg	-	-	≤5	≤5	-	≤10	-
Iodine Number	≤120	≤120	≤115	≤115	-	≤125	-
Distilation, %95, °C	-	-	≤360	-	≤360	-	≤360
Flash point, °C	≥120	≥100	≥100	≥110	≥100	≥100	≥130

Table 3.2. Continued

Water Content, mg/kg	≤500	-	≤200	≤300	≤700	≤300	≤0,05%
Phosphorus, mg/kg	≤10	≤20	≤10	≤10	≤10	≤10	≤0,001 mass%
Not determined Components, mg/kg	≤24	-	-	≤20	-	≤20	-
Sulfur, Weight % (mg/kg)	≤10	≤0,02	-	≤0,01	≤0,01	≤0,001	≤0,05
C18:3 and High Unsaturated FA, Weight %	-	≤15	-	-	-	-	-
C(x:4) and High Unsaturated FA, Weight %	≤1	-	-	-	-	-	-
Oxide Ash, Weight %	-	-	-	-	≤0,01	≤0,01	-
Sulfate Ash, Weight %	≤0,02	≤0,02	-	≤0,03	-	-	≤0,02
Methanol, Weight %	≤0,2	≤0,2	≤0,1	≤0,3	≤0,2	≤0,2	-
Linoleic Acid, Weight %	≤12	-	-	-	-	-	-
MG, Weight %	≤0,8	-	≤0,8	≤0,8	≤0,8	≤0,8	-
DG, Weight %	≤0,2	-	≤0,2	≤0,4	≤0,2	≤0,1	-
TG, Weight %	≤0,2	-	≤0,2	≤0,4	≤0,1	≤0,1	-
Free Glycerine, Weight %	≤0,02	≤0,02	≤0,02	≤0,02	≤0,02	≤0,02	≤0,02
Total Glycerine, Weight %	≤0,25	≤0,24	≤0,25	≤0,25	-	-	≤0,24
Ester, Weight %	≥96,5	-	≥96,5	-	≥98	≥98	-
Group I Metals (Na,K), mg/kg	≤5	-	-	-	-	-	-
Group II Metals (Ca,Mg), mg/kg	≤5	-	-	-	-	-	-
Oxidation Stability, h, 110 °C	Minimum . 6 hrs	-	-	-	-	-	-

Source: (Mofijur et al., 2012; Karaosmanoğlu, 2002).

Table 3.3 displays some important biodiesel parameters and the recommended methods of the ASTM and EN14214 standards which are used in the analysis of some of the contaminants and the maximum levels anticipated in a good biodiesel in these standards, (EN14214 and ASTM D 6751) (Prah, 2010).

Table 3.3. ASTM D6571 and EN14214 standards for biodiesel

Property	Test method ASTM [EN14214]	Limits ASTM [EN14214]	Units ASTM [EN14214]
Flash point (closed cup)/	ASTM [EN14214]	ASTM [EN14214]	°C [% mol/mol]
methanol content			
Water and sediment	D2709	0.050max [500max]	Volume % [mg/kg]
Kinematic viscosity	D445	1.9-6.0 [3.5-5.0]	mm ² /s
Sulphated ash	D874/I SO 3987	0.020 max [0.02max]	mass% [% mol/mol]
Iodine value	*NA [EN14111]	[120max]	% mass
Copper strip corrosion	D130 [EN ISO 2160]	No. 3 max [1]	[degree of corrosion]
Cetane number	D613 [EN ISO 5165]	47 min [51min]	
Cloud point/CFPP	D2500	*NSV	°C
Carbon residue	D4530	0.05 max [0.30max]	Mass % [mol%]
Acid number/Value	D664 [EN14204]	0.50 max	mgKOH/g
Free glycerin	D6584	0.02 max	Mass%
Total glycerin	D6584	0.240 max [0.25max]	Mass%
Linolenic acid content	NA [EN14103]	12.0max	%(mol)
Content of FAME with ≥ double bonds		1max	%(mol)
Ester content(min)	NA [EN14103]	96.5min	%(mol/mol)

Source: (Prah, 2010)

*NA-not applicable, *NSV-No specific value.

4. LITERATURE REVIEW OF BIODIESEL PRODUCTION FROM SAFFLOWER OIL

In the last years, numerous studies have been conducted on the safflower oil to investigate their conversion into biodiesel. (Nosheen, Bano, & Ali, 2014) studied the physicochemical characterization and authentication of safflower oil biodiesel yield by advanced tools. The biodiesel from safflower oil was obtained using base catalyzed transesterification reaction. Under conditions of 1:6 oil/methanol molar ratio, 0.5% NaOH concentration, 65°C reaction temperature and 1 hr reaction duration, the maximum biodiesel yield reached 97.84%.

Safflower oil was extracted by soxhlet apparatus. The maximum amount of extracted oil was 29%. Transesterification reaction achieved using a two-neck round bottom flask and under conditions of 6:1 methanol to oil molar ratio, 1.0% w/w KOH concentration, 55°C reaction temperature and 6 hr reaction period reported as the optimum conditions for biodiesel production with FAME conversion 96.1% (Tahvildari et al., 2013).

(Thomas, Birney, & Auld, 2013) studied the optimizing esterification of safflower, cottonseed, used cottonseed and castor oils. The molar ratios of safflower, cottonseed and castor to methanol was 1:3 while it was 1:4 of used cottonseed to methanol in the presence of NaOH and KOH as catalyst with reaction temperature 50°C for 2-3 hours. The optimum yield percent for SaME, CSME, UCSME and CME was 82, 83, 60 and 93.4% respectively. The same procedure was used with ethyl esters taking into account the change in molar ratios to 1:6, 1:8 and 1:10 with optimum yield percent 85, 87 and 74% for SaME, CSME and CME respectively.

(Thomas, Birney, & Auld, 2012) studied the transesterification and viscosity reduction of castor oil esters by the addition of biodiesel, safflower oil esters and additives. The reaction was conducted with 1:3 and 1:6 molar ratio of oil to methanol and ethanol in the presence of NaOH and KOH at 50°C for 1 hr to produce CME. The same conditions were used in the preparation of safflower ester except the reaction temperature which was at 70°C. The obtained biodiesel

analyzed with ^1H NMR and the CME achieved high percent yield 92.3% than SaME 79.8%. The initial viscosity of CME was found 13.5 times higher than No. 2 diesel which was 0.0295 and 0.0047 for CME and SaME respectively.

(Hamamci, Saydut, Tonbul, Kaya, & Kafadar, 2011) studied the production of biodiesel via transesterification from safflower seed oil. In this study, methanol to oil molar ratio, catalyst concentration, reaction duration and reaction temperature were investigated. Under conditions of 6:1 methanol/oil molar ratio, 0.5% w/w NaOH concentration, 2 hr reaction period and 65°C reaction temperature, the best SOME conversion value was 93%.

(Sagiroglu et al., 2011) studied the biodiesel productivities of different vegetable oils by acidic catalysis. Canola, sunflower, corn, safflower, waste sunflower, soybean, crude hazelnut and crude olive oils selected to react with the known ratio of methanol in the presence of hydrogen chloride 1.85 % (w/v) as catalyst. The mixture was stirred vigorously at 25 and 100°C for 1 hour. Sunflower reported as the highest biodiesel productivity with conversion 95.2% followed by safflower, soybean, canola, waste sunflower, olive, hazelnut and corn with conversions 94.3, 94.2, 93.7, 90.4, 85.3, 83.4 and 83,3 respectively.

(Duz, Saydut, & Ozturk, 2011) studied the alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. Transesterification reaction was carried out under microwave heating to study the impact of microwave irradiation on the process. Reaction mixture was irradiated using 300 w power start labstation microwave system. They achieved high conversion of methyl ester 98.4% using parameters of 10:1 methanol to safflower oil molar ratio, 1.0% w/w NaOH concentration, 60°C reaction temperature and 6 min reaction duration.

(Rashid & Anwar, 2008) studied the production of biodiesel through Base-Catalyst transesterification of safflower oil using an optimized protocol. In this study, the effect of oil/methanol molar ratio, catalyst types and their concentrations, reaction temperature, rate of stirring and reaction duration were investigated. The conditions of 1:6 oil/methanol molar ratio; 1.00% NaOCH_3

concentration; 60°C reaction temperature; 600 rpm rate of stirring; 120 min reaction period offered the best conditions with a high ester yield (98%).

(Meka, Tripathi, & Singh, 2006) studied the synthesis of biodiesel fuel from safflower oil using various reaction parameters. The impact of methanol/oil molar ratio, catalyst concentration and reaction temperature were studied. The analytical procedure carried out by Gas Liquid and Thin Layer chromatography and it has been found that 6:1 molar ratio of methanol to oil, 2% w/w NaOH concentration and 60°C reaction temperature were the optimize parameters for biodiesel production from safflower oil with maximum yield 96.8%.

5. EXPERIMENTAL STUDIES AND RESULTS

5.1. Materials

The reagents used in this study as reference materials in standard solutions were purchased from Sigma-Aldrich which are: Ethyl linoleate; Glyceryl trilinoleate; Linoleic acid; 1,3-Dilinoleoyl-rac-glycerol; 1-Linoleoyl-rac-glycerol. Chromarods SIII were from SES GmbH – Analysesysteme, Germany. TLC plates polygram silica gel 20×20 cm (0.2 mm gel) were from Macherey-Nagel, Germany. The refined safflower oil purchased from Tohum Tarim Company, Izmir, Turkey.

Ethanol as alcohol and NaOCH₃ as catalyst for transesterification reaction were purchased from Sigma-Aldrich. The developing solvents which used as mobile phase in TLC (hexane, diethyl ether and formic acid) were also purchased from Sigma-Aldrich. The reagents which were used to determine the preliminary experiments values of safflower oil were from Sigma-Aldrich and Merck.

5.2. Preliminary Experiments of Safflower Oil

5.2.1. Acidity determination

The acid value (AV) is an important indicator of vegetable oil quality (Kardash & Tur, 2005). "This method determines free (uncombined) fatty acids, which are calculated in terms of mg of KOH necessary to neutralize the FA in 1 g of test sample" (Firestone, 2009) (AOCS official method F 9a-44).

The experiment began with preparing 0.5 N KOH, phenolphthalein (phph) indicator and neutralized alcohol, then 10 g of safflower oil poured into 250 ml conical flask followed by 50 ml neutralized alcohol, 25 ml diethyl ether, 5 drops phph and titrated with 0.5 N KOH. The calculated results are:

$$\begin{aligned} \text{Acidity as mg KOH/g} &= \frac{\text{volume, ml of alkali} * 28.05}{\text{mass of test portion, g}} = \frac{0.4 * 28.05}{10} \\ &= 0.8 \text{ mg KOH/g} \end{aligned}$$

$$\begin{aligned}
 & \text{Free fatty acid, \%} \\
 &= \frac{(\text{volume, ml of alkali} * N \text{ of KOH} * \text{molecular weight of fatty acid})}{10 * \text{mass of test portion, g}} \\
 &= \frac{0.4 * 0.5 * 885.47}{10 * 10} = 1.77 \%
 \end{aligned}$$

5.2.2. Peroxide value (PV) determination

“This method determines all substances, in terms of milliequivalents of peroxide per 1000 grams of test sample that oxidize potassium iodide under the conditions of the test. The substances are generally assumed to be peroxides or other similar products of fat oxidation” (Firestone, 2009) (AOCS official method Cd 8b-90).

Principally, the safflower oil sample was treated in solution with a mixture of acetic acid and chloroform and then with a solution of potassium iodine, where the liberated iodine was titrated with sodium thiosulfate standard solution. Experimentally, the sodium thiosulfate, potassium iodine solution and acetic acid chloroform mixture (AA-CHL) by ratio of (3:2) were prepared, then, 5.0g of safflower oil weighted and poured into 250 ml conical flask followed by 30 ml (AA-CHL) mixture and swirled until the test portion was dissolved. Using a suitable volumetric pipet, 0.5 ml potassium iodide solution was added and the solution allowed to stay for exactly 1 min and then 30 ml of distill water was added immediately. In the next step, the solution titrated with 0.1 M sodium thiosulfate until the yellow iodine color has almost disappeared. 0.5 ml of starch indicator solution was added and the titration continued with constant agitation specifically near the end point to release all of the iodine from the solvent layer, then, thiosulfate solution dropwise was added until the blue color completely disappeared.

$$\begin{aligned}
 & \text{Peroxide Value (milliequivalents peroxide/1000g test portion)} \\
 &= \frac{(S - B) * M * 1000}{\text{mass of test portion g}} = \frac{(0.9 - 0.7) * 0.1 * 1000}{5} \\
 &= 4 \text{ meq/kg}
 \end{aligned}$$

5.2.3. Iodine value (IV) determination

“The iodine value is a measure of the unsaturation of fats and oils and is expressed in terms of the number of centigrams of iodine absorbed per gram of sample (% iodine absorbed)” (Firestone, 2009) (AOCS official method Cd 1-25).

To obtain the iodine value, 0.16 g of the sample weighted and poured into 500 ml iodine flask. 15 ml of carbon tetrachloride was added to the iodine flask and then shaken to guarantee that the sample entirely dissolved. Then, 25 ml of wijs solution was measured using the pipet and appended to the mixture above with keeping swirl. The flask stored in a dark place under temperature $23\pm 1^{\circ}\text{C}$ for 30 min. After this period, 20 ml of potassium iodide (KI) solution was added to the flask followed by 100 ml of distilled water. Eventually, the solution titrated with 0.1 N sodium thiosulfate solution with constant strong shaking until the yellow color has almost disappeared. Thereafter, 2 ml of starch indicator solution was added and the titration continued until the blue color perfectly disappeared (colorless). The blank is the other prepared with the same procedure and the results determined from:

$$\text{Iodine Value} = \frac{(B - S) * N * 12.69}{\text{mass, g of sample}} = \frac{(26.8 - 9) * 0.1 * 12.69}{0.16} = 141.17$$

Where:

B = volume of titrant, ml of blank

S = volume of titrant, ml of sample

N = normality of sodium thiosulfate solution

5.2.4. Saponification value (SV) determination

“The saponification value is the amount of alkali necessary to saponify a definite quantity of the test sample. It is expressed as the number of milligrams of potassium hydroxide (KOH) required to saponify 1 gram of the test sample” (Firestone, 2009) (AOCS official method Cd 3-25).

To investigate the saponification value in safflower oil, 1 gram oil was measured and poured into 250 mL ground neck Erlenmeyer flask followed by 25 ml alcoholic KOH. The mixture was allowed to boiling softly until the test portion was entirely saponified under reflux of condenser for 35 min. 1 ml of phenolphthalein indicator was added and titrated with 0.5 N HCl until the pink color completely disappeared, then, the required volume of 0.5 N HCl was recorded from burette. The blank was also prepared in the same procedure above without sample (oil). Saponification value was determined from:

$$\begin{aligned} \text{Saponification Value} &= \frac{(B - S) * M * 56.1}{W} = \frac{(17.3 - 10.8) * 0.5 * 56.1}{1} \\ &= 182.3 \text{ mg/g} \end{aligned}$$

Where:

B = volume of 0.5 N HCl required to titrate blank, ml

S = volume of 0.5 N HCl required to titrate test portion, ml

M = molarity of HCl solution

W = mass of test portion, g

$$\begin{aligned} \text{Ester Value} &= \text{Saponification Value} - \text{Acid Value} = 182.3 - 0.8 \\ &= 181.5 \text{ mg/g} \end{aligned}$$

$$\% \text{ Ester Content} = \frac{\text{Ester Value} * \text{MW of Ester}}{10 * 56.1} = \frac{181.5 * 293.8}{10 * 56.1} = 95.05 \%$$

5.2.5. Moisture content

A certain amount of oil sample was weighted and reported as W1 then was dried in the oven to expel the internal moisture. After drynig, the weight of sample taken as W2 (Folaranmi, 2013). The moisture content calculated from:

$$\% \text{ Moisture Content} = \left(\frac{W1 - W2}{W1} \right) * 100 = \left(\frac{10 - 8.8}{10} \right) * 100 = 0.12 \%$$

Where:

W1 = the weight of sample in gram before drying.

W2 = the weight of sample in gram after drying.

5.2.6. Specific gravity

To determine specific gravity of safflower oil, 25 ml dry and clean density bottle was taken and weighed w_0 , then filled with oil and reweighed to give w_1 . The oil replaced with water after cleaning and drying the same bottle and weighed to give w_2 (Folaranmi, 2013). Specific gravity calculated from:

$$\text{Specific gravity} = \left(\frac{w_1 - w_0}{w_2 - w_0} \right) = 0.917$$

5.2.7. Density

To determine density of safflower oil, 50 ml dry and clean beaker was taken and placed on the sensitive balance then zero key was pressed to neglect the beaker weight. After that, the beaker filled with oil to the mark and the recorded weight reported as (w). Density determined from:

$$\text{Density at } 15^\circ\text{C} = \frac{w}{v} = \frac{42.2}{50} = 0.84 \text{ g/ml} \text{ \& at } 40^\circ\text{C} = \frac{40.9}{50} = 0.82 \text{ g/ml}$$

Where:

w = weight of the sample in gram (g)

v = the beaker volume (ml)

5.3. Calibration of Standards with TLC/FID

For the calibration of standards, the results of the studies of (Indrasena, Henneberry, Barrow, & Kralovec, 2005), (Fedosov, Brask, & Xu, 2011) and (Freedman, Pryde, & Kwolek, 1984) were considered. The chromatograms were pre-scanned under the conditions of FID measurement condition where shown in Table 5.1. A mixture of standards of Ethyl linoleate (Ethyl Ester, EE); Glycerol trilinoleate (Triglyceride, TG); Linoleic acid (Free Fatty Acid, FFA); 1,3-Dilinoleoyl-rac-glycerol (Diglyceride, DG); 1-Linoleoyl-rac-glycerol (Monoglyceride, MG) were prepared in a various concentrations within range of

(3-15) mg/ml. Micro-dispenser used to spot each sample solution on the rods. A 1 μ L selected as the appropriate spotting size for better quantification. The rod holder (Figure 5.1) left for 5 min in the air temperature after spotting. Subsequently, rods were placed in a glass developing tank (Figure 5.2) for customary TLC and developed in Hexane (HE)/Diethyl Ether (DE)/Formic Acid (FA) (85 : 15 : 0.04) for 25 ± 2 min and then dried for 3 min in the air oven at $118 \pm 2^\circ\text{C}$ (for each developing with solvents). The chromarods (Figure 5.3) were scanned by flame ionization detector FID (Figure 5.4) used hydrogen flow rate (160 ml/min), air flow rate (2 L/min) and scan speed (30 sec/rod). The area response of each standard plotted versus the weight ratios for standard solutions. The intercept and slope of the five compounds were determined as shown in Figures (6.1 to 6.5).



Figure 5.1. Rod Holder



Figure 5.2. Developing Tank



Figure 5.3. Chromarods



Figure 5.4. Iatroscan MK-6s

5.4. Operating Conditions and Instrumentation

Analyses were accomplished with an Iatroscan MK6-s analyzer (Iatron laboratories, Tokyo, Japan). The set values for TLC/FID analyzer are determined as explained in Table 5.1.

5.4.1. Iatroscan MK-6s

Device is equipped with analysis and detection technology with combination Thin Layer Chromatography and Flame Ionization Detector TLC/FID. Iatroscan MK-6s analytical system used in several application fields such as pharmaceutical industries, carbon and crude oil industries, carbon products, biochemistry, biotechnology, environmental pollution, plant breeding, forestry, food industries, fishery...etc. Figure 5.5 shows the Iatroscan MK-6s analysing system for TLC/FID.

Table 5.1. Developing system parameters and FID measurement conditions for TLC/FID analyzer

Developing System		FID Measurement Condition	
Sample Volume	1 μ L	Hydrogen Flow Rate	160 mL/min
Sample Composition	10 mg Sample/1 ml Hexane	Air Flow Rate	2.0 L/min
Developing Solvent	Hexane: Diethyl Ether: Formic Acid (85: 15: 0.04)	Scan Speed	30 sec/scan
Developing Time	25 min		
Drying System	5 min in the air temperature after spotting and 3 min in the air oven at 120°C after each developing with solvent.		

5.4.1.1. The advantages of iatroscan system are:

- The system is developed to accommodate 10 chromatids at the same time.
- The chromatids are flexible to use for 100 times again.
- Time of analyzing take 20-30 min depending on method.
- Used in many application fields such as crude oil and carbon industry, biotechnology, biochemistry, food industry and pharmaceutical industry.

Source: (TLC-FID / FPD analyser Iatroscan MK6(s), 2015).

URL: http://www.ses-analysesysteme.de/IATROSCAN_UK.htm

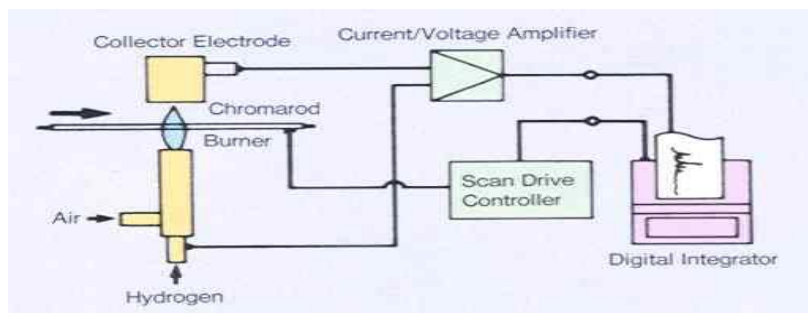


Figure 5.5. The Iatroscan MK-6s Analysing System for TLC with FID (“BIONIS,” 2014).

5.5. Base Catalyzed Transesterification Reaction

For transesterification reaction, the results of (Rashid & Anwar, 2008), (Tahvildari et al., 2013), (Ilkılıç, Aydın, Behcet, & Aydın, 2011), (Thomas et al., 2012), (Meka et al., 2006), (Thomas et al., 2013), (Mihaela, Josef, Monica, & Rudolf, 2013), (Nosheen et al., 2014), (Karaosmanoğlu, Akdağ, & Cigizoğlu, 1997), (Işler et al., 2010), (Ullah, Bano, & Ali, 2013), (Folaranmi, 2013), (Berchmans & Hirata, 2008), (Labib et al., 2013), (Ahmed, Nazar, Ali, Rana, & Khan, 2015), (Silitonga, Chyuan, Mahlia, Masjuki, & Chong, 2014), (Kywe & Oo, 2009), (Mazo & Rios, 2010), (Yin et al., 2015) and (Hamamci et al., 2011) were considered. In this step, NaOCH_3 catalyst concentration was investigated. Throughout the experiments, a various oil/ethanol molar ratios (1:3, 1:6 and 1:9) were applied while the reaction temperature ($65 \pm 1^\circ\text{C}$), agitation rate (600 rpm) and reaction duration (60 min) were kept constant. The investigation was carried out in the various amounts of NaOCH_3 (0.25%, 0.50%, 0.75% and 1.00%).

The oil poured into reactors and heated briefly at $65 \pm 1^\circ\text{C}$, then, the NaOCH_3 was dissolved in ethanol and poured into reactors (Figure 5.6). The timer was set at 1hr and switched on with the beginning of the reaction. Numerous Samples were taken from the mixture at different intervals (2, 5, 8, 10, 15, 20, 30, 40, 50 and 60 min) during the reaction into the test tubes. Using a sensitive balance, 0.1 mg mixture was measured and dissolved in 1 mL hexane, then, a 1 μL was applied in the rods using micro-dispenser. The rod holder with spotted rods was left for 5 min in the room temperature then developed in the developing tank using developing system mentioned in Table 5.1. After developing, the rods

exposed to the oven heat ($118\pm 2^{\circ}\text{C}$) for 3 min and eventually they were placed in the Iatroscan MK-6s analyzer. With applying the FID measurement condition described in Table 5.1, the rods were scanned and the ester contents were calculated. Biodiesel and glycerin separation by gravity is clearly shown in Figure 5.7, where the Figure 5.8 shows the lower phase (row glycerin) after separation.

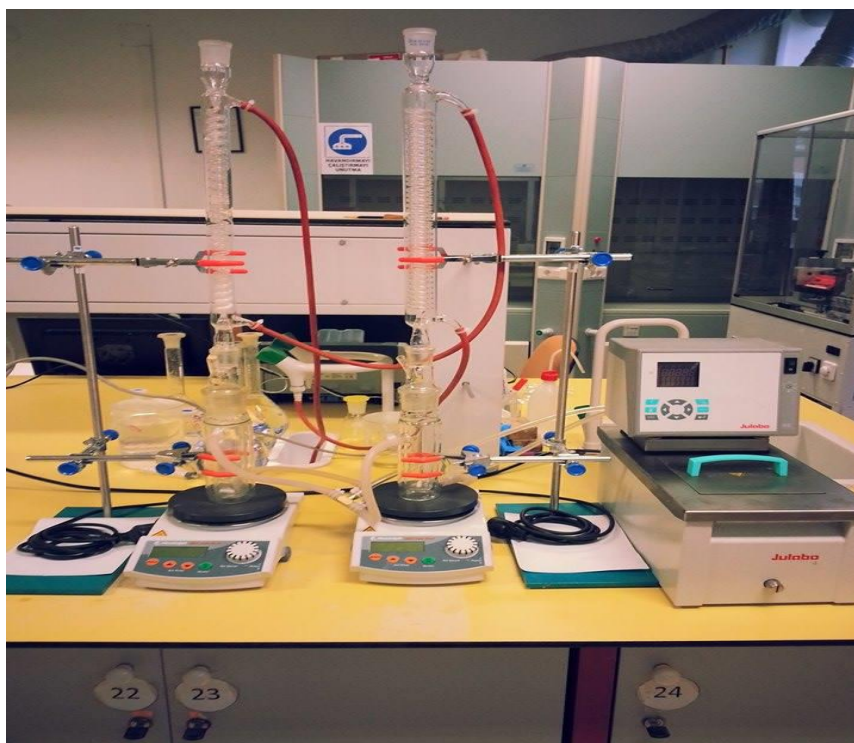


Figure 5.6. The Experimental Setup



Figure 5.7. Biodiesel and Glycerin
Phase Separation



Figure 5.8. Glycerin

6. RESULTS AND DISCUSSIONS

6.1. Properties and the Preliminary Experiments

Properties and the preliminary experiments of safflower oil were determined in the laboratory and presented in Table 6.1 below:

Table 6.1. Properties of Safflower Oil

Property	Safflower Oil
Acid Value, mg KOH/g	0.8
Peroxide Value, meq/kg	4
Iodine Value, gI ₂ /100g	141.2
Saponification Value, mg KOH/g	182.3
Density, 15°C, g/cm ³	0.84
40°C, g/cm ³	0.82
Moisture Content, %	0.12
Specific Gravity at 25°C	0.917
Kinematic Viscosity, 40°C, mm ² /s	30
Color	Golden Yellow

6.2. Calibration Standards

The calibration curves for the 5 standard solutions; ME, TG, FFA, DG, and MG has been drawn as well as the intercepts and slopes derived from these plots as shown in Figures (6.1 to 6.5). Each solution containing a homogeneous mixture of standards and each data point is an average result of 10 analyses.

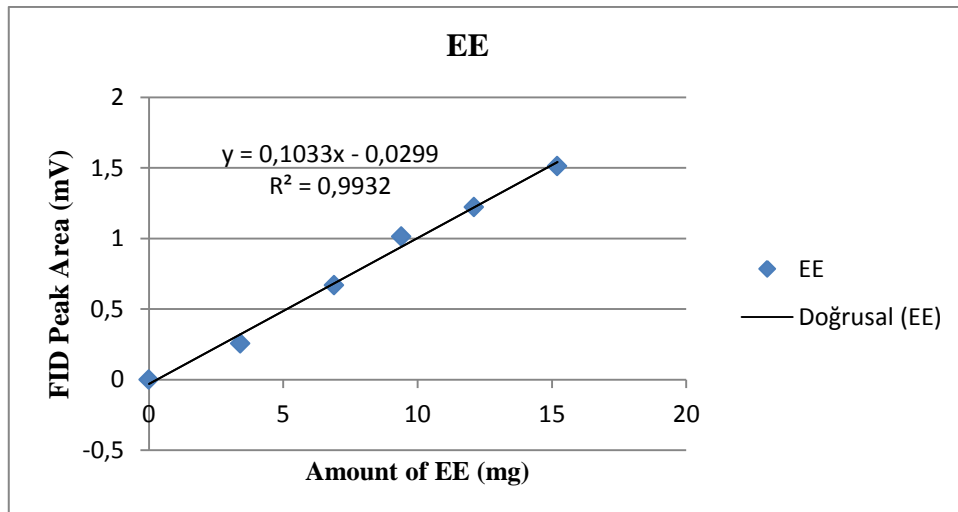


Figure 6.1. Calibration curve for Ethyl Ester (EE)

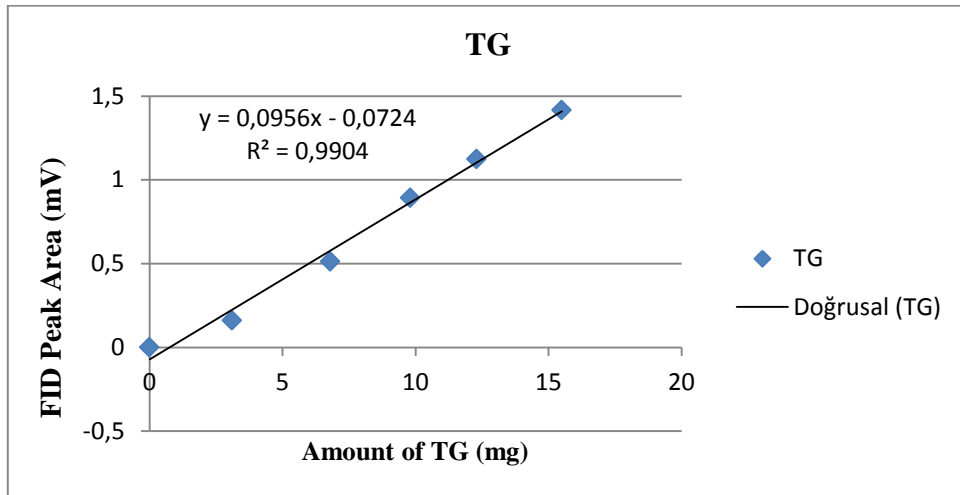


Figure 6.2. Calibration curve for Triglycerides (TG)

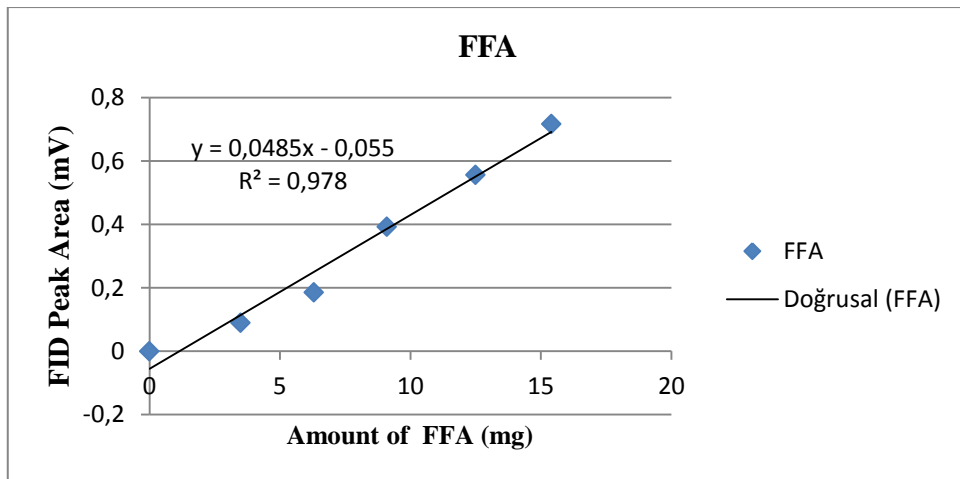


Figure 6.3. Calibration curve for Free Fatty Acids (FFA)

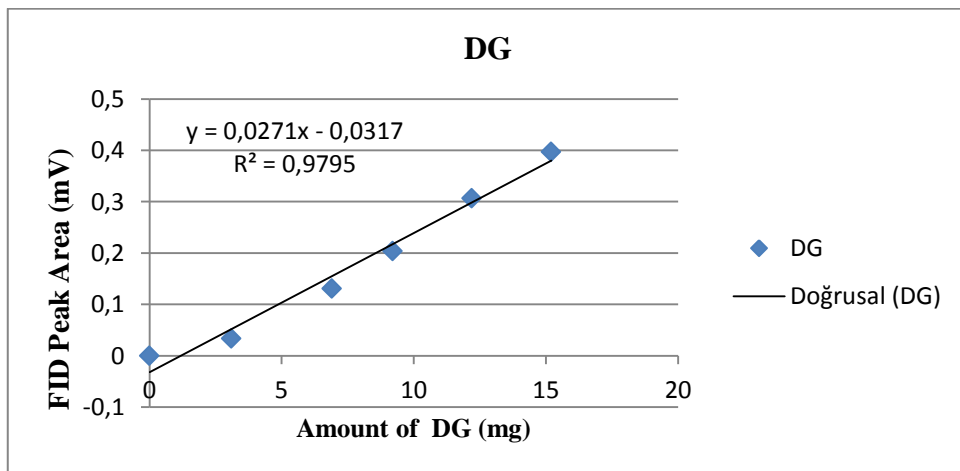


Figure 6.4. Calibration curve for Diglycerides (DG)

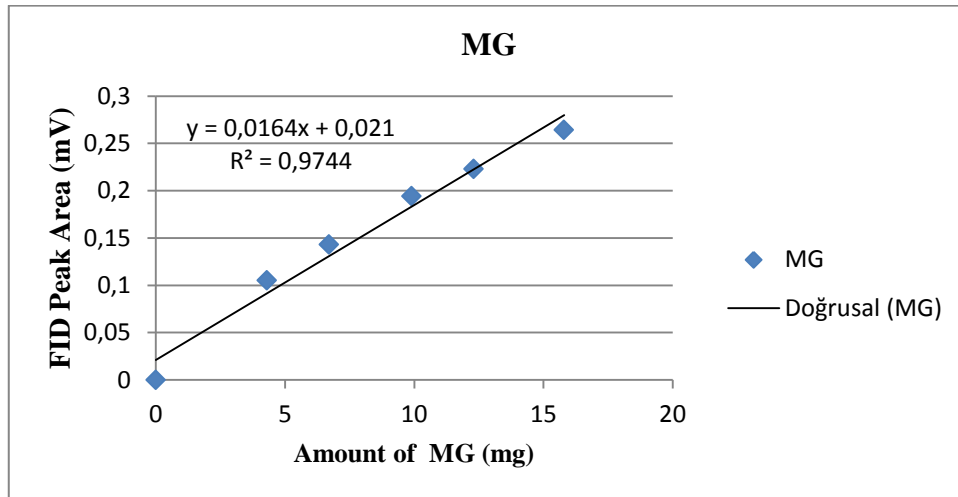


Figure 6.5. Calibration curve for Monoglyceride (MG)

6.3. Ester Content of Biodiesel from Safflower Oil

The areas of ME, TG, FFA, DG and MG has been painted and reported using calculate theoretical plates function in the iatrosan MK6-s environment and each sample was separated individually (Figure 6.6). By taking into account the area of internal standards peaks, mass of samples, slope and intercept (which was evaluated from calibration standards method with the experimentally obtained areas peaks), the ester content of ethyl esters was determined. Figures (6.7 to 6.10) illustrates the ester contents of SO to SOEE.

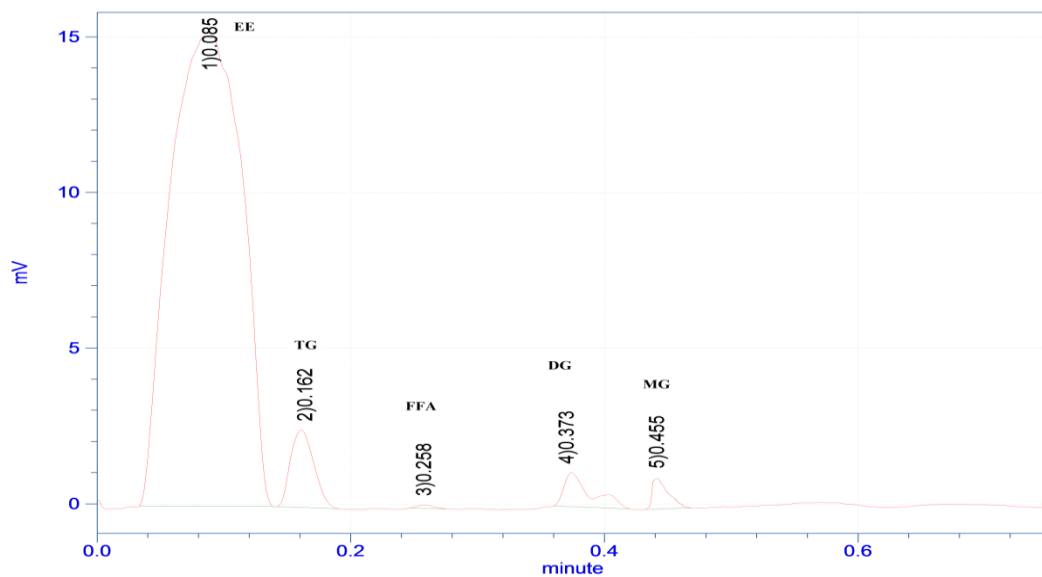


Figure 6.6. Ethyl Ester (EE), Triglycerides (TG), Free Fatty Acids (FFA), Diglycerides (DG) and Monoglycerides (MG) Areas in the Iatrosan MK-6s Environment.

The recorded profiles were analyzed with μ 7Data Station, SIC system instruments CO., LTD, ver. 1.5A-E. All results was calculated based on this data.

The linear regression equations were obtained from area and weight ratios of standard solutions plots (Freedman et al., 1984).

$$Ac/As = a + b \cdot (Wc/Ws) \quad [1]$$

Where:

Ac = the area of the compound,

As = the area of the internal standard,

a = the intercept,

b = the slope,

Wc = the weight of the compound and,

Ws = the weight of the internal standard.

All these information was used in equation [2] after determining a and b for each compound in the standard solutions to calculate the compound weight:

$$Wc = [(Ac/As - a) / b] \cdot Ws \quad [2]$$

After obtaining the weight percentage of each compound, the percentage composition were calculated from:

$$\text{Compound Weight \%} = (Wc / \sum Wc) \cdot 100 \quad [3]$$

6.3.1. Effect of the catalyst concentration on the ester content of safflower oil to SOEE

The base catalyzed transesterification was applied in the presence of NaOCH₃ as catalyst. The results of all experiments are described in Figures (6.7-6.9). Obviously, the concentration of the catalysts was extremely significant parameter thereby greatly affected the transesterification process. In this study, the concentrations which has been selected were 0.25%, 0.50%, 0.75% and 1.00%

(w/w) whilst the oil/methanol molar ratios were 1:3, 1:6 and 1:9, reaction temperature $65 \pm 1^\circ\text{C}$, rate of stirring 600 rpm and reaction time 60 min. First of all, 0.25% of catalyst was chosen with the other parameters to investigate the oil ester content. Figure 6.7 shows the effect of the catalyst concentrations with 1:3 oil/ethanol molar ratio on the ester content as a function of reaction time. It's clearly that the ester content reached only 38.62%, 55.12% and 46.32% when using 1:3, 1:6 and 1:9 oil/ethanol molar ratios respectively.

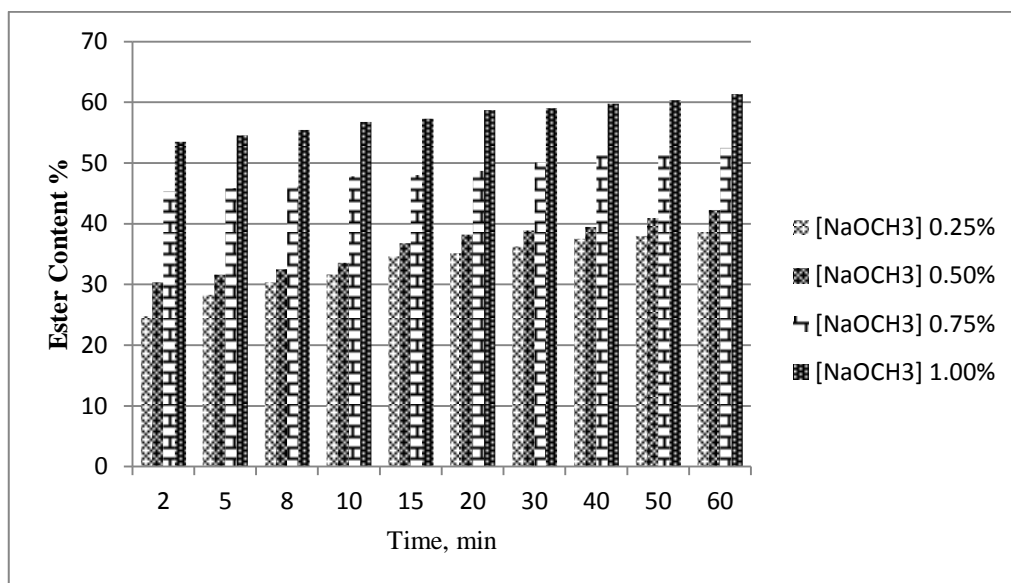


Figure 6.7. Effect of the “0.25%, 0.50%, 0.75% and 1.00% (w/w) NaOCH₃ concentration” on the SOEE ester content (1:3 oil/ethanol molar ratio, 600 rpm rate of stirring, and 65°C reaction temperature).

The ratio was raised to 0.50% for catalyst and they noticed that there was a slight increase in the ester contents reported as follows: 42.24%, 71.80% and 61.91% in the same order. The ester contents increased noticeably and reached 52.48%, 87.74% and 82.61% when 0.75% of the catalyst was applied. According to these results, increasing of catalyst amounts promoted the reaction to form more products and indicated that the reaction has not reached equilibrium yet. On the other hand, the excess amounts cannot achieve high ester content because the reaction will be already reached equilibrium.

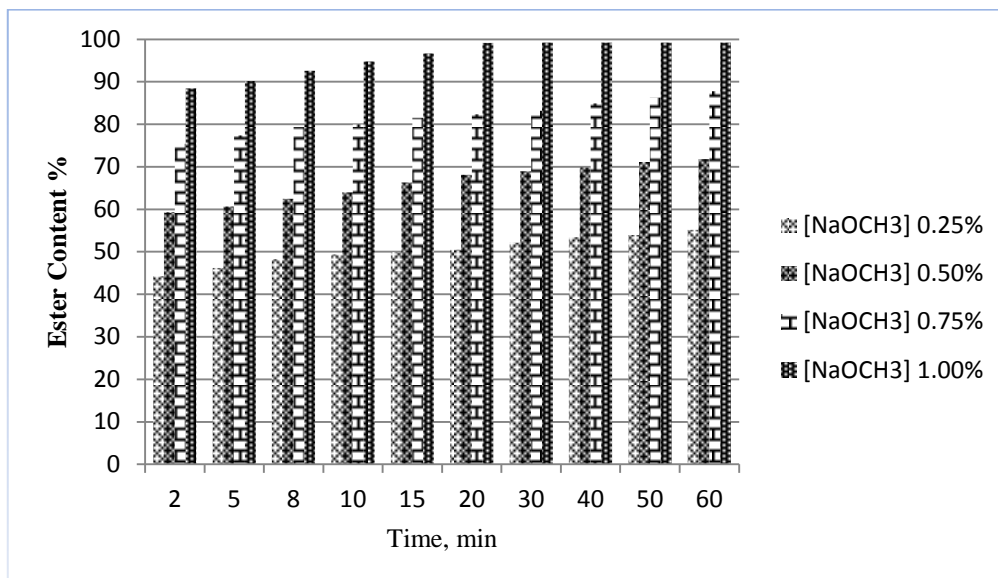


Figure 6.8. Effect of the “0.25%, 0.50%, 0.75% and 1.00% (w/w) NaOCH₃ concentration” on the SOEE ester content (1:6 oil/ethanol molar ratio, 600 rpm rate of stirring, and 65°C reaction temperature).

Eventually, the catalysts concentration was set as 1.00% and the ester content reaches 99.16% using NaOCH₃ after 20 min as seen in Figure 6.8 under conditions of (rate of stirring 600 rpm, reaction temperature 65±1°C and oil/ethanol molar ratio 1:6) while the ester content percentage using 1:3 and 1:9 with the same other conditions reached 61.34% and 90.23% respectively.

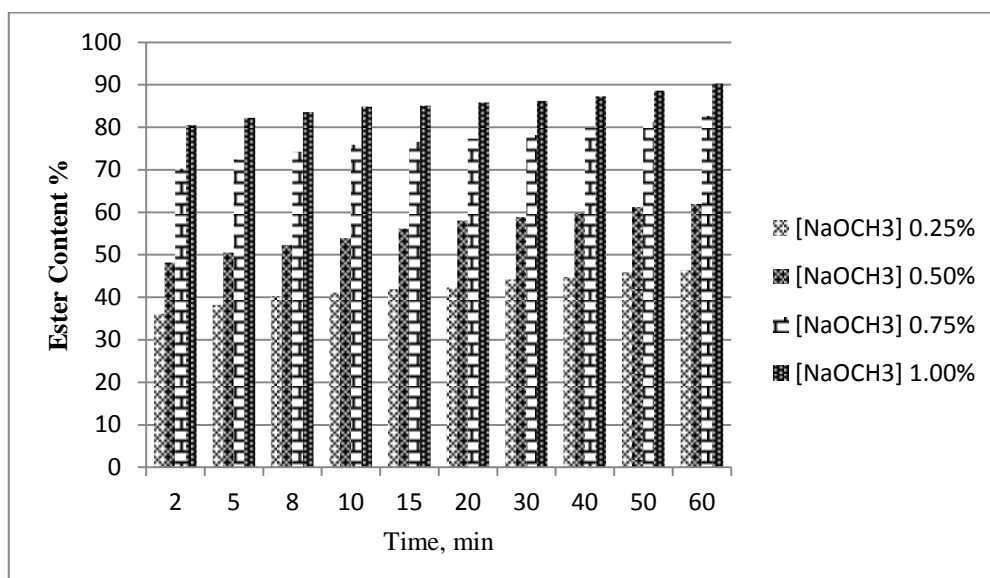


Figure 6.9. Effect of the “0.25%, 0.50%, 0.75% and 1.00% (w/w) NaOCH₃ concentration” on the SOEE ester content (1:9 oil/ethanol molar ratio, 600 rpm rate of stirring, and 65°C reaction temperature).

6.3.2. Optimization of the oil/ethanol molar ratio

The ethanolsis of safflower oil was accomplished in three experiments where the oil/ethanol molar ratios were (1:3, 1:6 and 1:9). Because of the irreversibility of transesterification reaction, excess amounts of ethanol was applied to shift the equilibrium towards products side which is result in high ester content. The effect of the ethanol concentration on SOEE production was investigated. Under the condition of 65°C reaction temperature, 600 rpm rate of stirring, and 1.00% (w/w) NaOCH₃ the high possible ester content (99.16%) of SOEE was obtained when the molar ratio of 1:6 was applied as clearly shown in Figure 6.10.

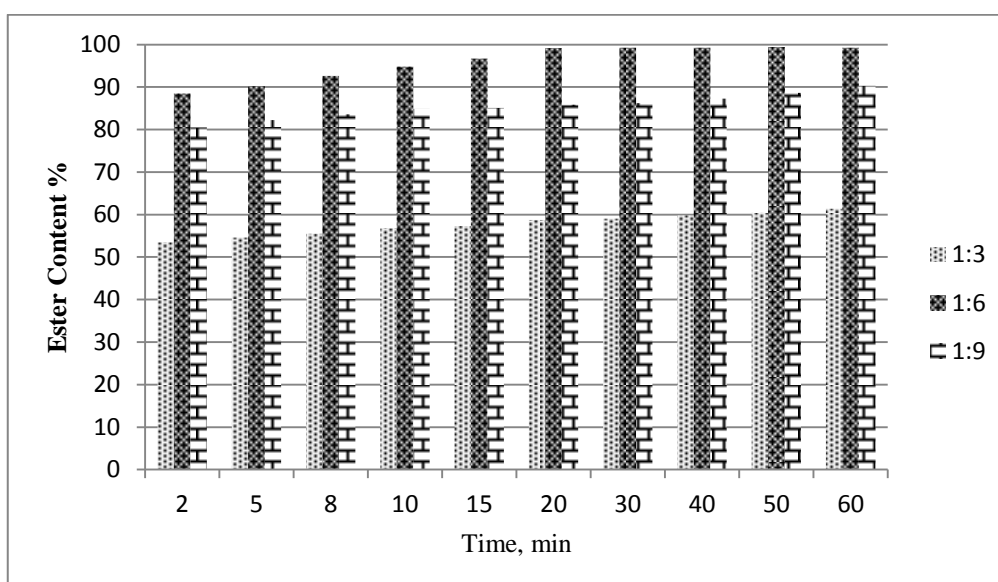


Figure 6.10. Effect of the 1:3, 1:6 and 1:9 oil/ethanol molar ratio on the SOEE ester content (1.00% (w/w) NaOCH₃ concentration”, 600 rpm rate of stirring, and 65°C reaction temperature).

By applying 1:3 oil/ethanol molar ratio, the ester content percent was just 61.34%. In the case of 1:9 oil/ethanol molar ratio, the separation of ester from glycerol was a problem because the excess ethanol obstructed the gravity decantation. Therefore, the ester content was diminished because of the presence of glycerol in the upper phase (Rashid & Anwar, 2008). Using lower oil/ethanol molar ratios (such as 1:6) is convenient in practical process, economically cheap and environmentally friendly.

7. CONCLUSIONS

Recently, biodiesel has become the best alternative to fossil fuel and fortunately, it is available sources to satisfy the fuel demands of the world. This abundance as a result of a tremendous numbers of vegetable oils which contribute in the biodiesel production. Safflower oil one of the leading worldwide vegetable oils based on this research and the previous research results that it has a good potential as an alternative diesel fuel. Moreover, the production of biodiesel from safflower oil offers a double-facet solution which represented in economic and environment.

To a large extent, transesterification was found the superior process for converting oils to their alcohol esters in the presence of catalysts. In this work, the Alkyl Esters Fatty Acids (Biodiesel) was obtained from safflower oil using the base catalyzed transesterification in the presence of NaOCH_3 as alkali catalyst with concentrations (0.25%, 0.50%, 0.75% and 1.00%) and oil/ethanol molar ratios (1:3, 1:6 and 1:9). The effect of these catalyst concentrations and oil/ethanol molar ratios on the ester content was investigated. The optimum reaction conditions were 1:6 oil/ethanol molar ratio, 1.00% (w/w) NaOCH_3 concentration, 600 rpm rate of stirring, $65 \pm 1^\circ\text{C}$ reaction temperature for 20 min.

Oil to Biodiesel ester content analyzed with iatroscan (TLC/FID) and the recorded profiles were analyzed with μ 7Data Station, SIC system instruments CO., LTD, ver. 1.5A-E. Under these conditions, the average biodiesel ester content was 99.2%.

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