

Thermal Cracking Approach Investigation to Improve Biodiesel Properties

Roghaieh Parvizesedghy, Seyyed Mojtaba Sadrameli

Abstract—Biodiesel as an alternative diesel fuel is steadily gaining more attention and significance. However, there are some drawbacks while using biodiesel regarding its properties that requires it to be blended with petrol based diesel and/or additives to improve the fuel characteristics. This study analyses thermal cracking as an alternative technology to improve biodiesel characteristics in which, FAME based biodiesel produced by transesterification of castor oil is fed into a continuous thermal cracking reactor at temperatures range of 450-500°C and flowrate range of 20-40 g/hr.

Experiments designed by response surface methodology and subsequent statistical studies show that temperature and feed flowrate significantly affect the products yield. Response surfaces were used to study the impact of temperature and flowrate on the product properties. After each experiment, the produced crude bio-oil was distilled and diesel cut was separated. As shorter chain molecules are produced through thermal cracking, the distillation curve of the diesel cut fitted more with petrol based diesel curve in comparison to the biodiesel. Moreover, the produced diesel cut properties adequately pose within property ranges defined by the related standard of petrol based diesel. Cold flow properties, high heating value as the main drawbacks of the biodiesel are improved by this technology. Thermal cracking decreases kinematic viscosity, Flash point and cetane number.

Keywords—Biodiesel, castor oil, fuel properties, thermal cracking.

I. INTRODUCTION

DIESEL, an important product of petroleum refineries, is an essential fuel for both diesel engines and home heating in developed countries. Diesel is produced by fractional distillation of C8–C25 hydrocarbon liquid from petroleum [1]. Regarding the world's decreasing petroleum reserves and environmental issues, renewable fuel sources alternative to petrol fuel are attracting attentions [2].

Biodiesel is an alternative diesel fuel which is officially defined as a “fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats” [3]. Mono-alkyl esters are produced through the transesterification in which, triglycerides in the vegetable oil or animal fat react with alcohol (mostly methanol) in the presence of catalyst and fatty acid methyl ester (FAME) as main product and glycerol as a valuable byproduct are produced. Biodiesel is also produced through non-catalytic process in which triglycerides react with alcohol in

supercritical conditions which poses safety issues [4]. The important issues of FAME (fatty acid methyl ester) based biodiesel are the inefficient performance of biodiesel at low temperature, low oxidative stability, low heating value and sometimes high kinematic viscosity required to be upgraded before use [5]. Nevertheless, transesterification has been commercialized and is used vastly in some countries because of its production simplicity and cost-competitiveness [1], [6].

One of the technologies for biodiesel upgrading is hydrotreating, the technology in which feedstock reacts with a source of hydrogen at high temperature and pressure in a catalytic reactor [7]. The final products are similar to the normal petrol based diesel, whereby the problematic and limiting cold flow properties of FAME biodiesel are minimized [8]. However, strong dependency to hydrogen source [9] beside the high energy consumption and raw material loss [8] seem to be the large drawbacks of hydrotreating.

Considering the technical limitations of aforementioned technology, the present study investigates the efficiency of pyrolysis technology on biodiesel properties upgrading. In pyrolysis, biomass is subjected to thermal cracking at high temperature in batch or continuous processes and in the absence of air [1]. In the case of using FAME biodiesel as feedstock through the pyrolysis, the methyl esters are cracked and the biodiesel is changed chemically. In this survey, the product of pyrolysis named as bio-oil and the separated diesel cut named as bio-diesel, in order to avoid dismissing with FAME based biodiesel.

Biodiesel decomposition starts from 270°C and molecules with shorter chain length and/or more saturated have higher thermal stability and tend to decompose later [10], [11]. The most important thermal decomposition reactions occurring with FAMES at high temperatures are summarized in Fig. 3. Decomposition of FAMES occurs at 275°C or above and consists of pyrolysis, isomerization, polymerization (Diels–Alder reaction) and reactions [11].

High-temperature pyrolysis and short residence time yields mixture of n-alkanes, alkenes and methyl esters of unsaturated fatty acids (Fig. 3, reactions 1a & 1b) with few amounts of aromatics [12].

Lower temperature pyrolysis and longer residence time, with a catalyst, leads to the formation of deoxygenated product, i.e., a mixture of linear alkanes and alkenes. Deoxygenation is attributed to decarboxylation, deketenization, and decarbonylation of FAMES (Fig. 3, Reactions 2 & 3). FAMES do not yield significant amounts of fatty acids (Fig. 3, reaction 3b), so a thermal process,

Roghaieh Parvizesedghy is with the Tarbiat Modares University, Tehran, Iran.

Seyyed Mojtaba Sadrameli is with Tarbiat Modares University, Tehran, Iran (corresponding author to provide phone: 98-21-82884902; fax: 98-21-82884902; e-mail: sadramel@modares.ac.ir).

maintaining the esters as a part of the products' mixture, should be possible [12].

Radical re-organization of methyl esters leads to the formation of high-MW hydrocarbons and dimethyl esters of dicarboxylic acids (Fig. 3, reactions 1d) combined with polymerization and formation of oligomers [12]. Dimers and/or polymers are produced through Diels–Alder reaction [9].

Previous research suggests that reactions resulting in cleavage of carbon–carbon bonds in triglycerides, known as cracking reactions, can produce chemical compounds that may be attractive in fuels and chemicals [15]. Thermal cracking of methyl ester of the canola oil was studied that proposed as a method to improve cold flow and stability properties of biodiesel fuels [13]. Therefore, this investigation is aimed at studying the properties of the bio-diesel and FAME based biodiesel to analyze the competency of thermal cracking as a method for improving the characteristic of the biodiesel. Thus, a series of thermal cracking conditions in a continuous reactor were evaluated to identify reaction conditions leading towards more yields of bio-oil and bio-diesel. Castor oil was used during the transesterification and the produced castor methyl ester was applied in the fast pyrolysis.

II. EXPERIMENTAL

A. Material

Refined castor oil was purchased from a food supply store (Tehran, Iran). Typical compositional analyses of castor oil as well as its physical properties are given in Table I. For transesterification of the oil, methanol 99% and sodium methoxide 95% were purchased from Dr.Mojalali Company (Tehran, Iran) and Fluka Company (St. Gallen, Switzerland) sequentially. For comparison between the properties of diesel with similar products, petrol based diesel which is produced in the Tehran Refinery was purchased from a petrol station.

TABLE I
COMPOSITION PROFILE OF CASTOR OIL

Component		Weight %
Pentadecyclic Acid	C15	7.38
Palmitic Acid	C16:0	3.51
Stearic Acid	C18:0	3.67
Oleic Acid	C18:1	1.38
Linoleic Acid	C18:2	12.15
Linolenic Acid	C18:3	1.03
Ricinoleic Acid	C18:1-OH	60.81
Gondoic Acid	C20:1	0.61
Nervonic Acid	C24:1	9.46

B. Experimental Setup and Procedures

Transesterification of the castor oil was performed in a batch reactor. The biodiesel was separated from the mixture of the products and feedstock (FAME biodiesel, glycerin, catalyst, soap and unreacted oil and methanol) through a sequential process of decanting, water washing and drying. Therefore, the pure biodiesel (98%) got ready for pyrolysis.

Thermal cracking experiments were performed in a continuous cracking system as shown in Fig. 1. The thermal cracking reactor was a cylinder made of quartz with a volume of 0.21 liter. An electrical cylindrical furnace externally heated the reactor up to the desired temperature and then the biodiesel was fed to the reactor from top. One dispenser found to be necessary to distribute the feed through the reactor uniformly. After thermal cracking of the feed, products in the form of gas left the reactor into a collecting container with a jacket of ice around. Thus, bio-oil was condensed and accumulated in the mentioned container and the non-condensable gases passed out through a flare system followed by a combustion gas relief.

Then, the bio-oil was distilled according to the standard method ASTM D86 [14] with the purpose of fractionating into three cuts as:

- IBP-160°C named as bio-gasoline
- 160-350°C named as bio-diesel
- More than 350°C named as heavy bio-oil

The experimental tests were designed by a 13 run central composite design (CCD) and two reaction parameters (thermal cracking temperature and flow rate of feed) were the main parameters. The expected responses were fuel properties of bio-diesel.

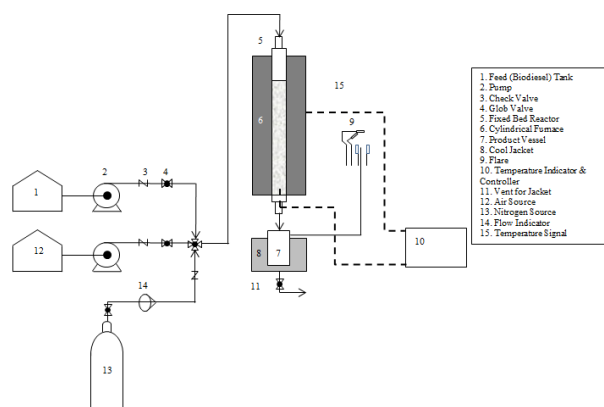


Fig. 1 Continuous thermal cracking system

C. Property Analysis

Bio-diesel properties including density, kinematic viscosity, cold flow properties, cetane index, heating combustion and flash point were analyzed based on the standard methods provided in Table II.

III. RESULTS AND DISCUSSION

A. Evaluation of the Thermal Cracking Diesel

The distillation curve (ASTM D86) of the, FAME based biodiesel, refinery diesel and final bio-diesel product is shown in Fig. 2. Comparison between the distillation curves of the FAME based biodiesel and refinery diesel shows significant differences between them which lead to differences in the properties of these products. Biodiesel is composed of much heavier molecules in comparison to the diesel as it is almost methyl ester of fatty acids, which have high boiling points.

The distillation curve of diesel and bio-diesel (this research) are very similar as the thermal cracking produced lighter molecules with less boiling points and by choosing initial and end boiling points of the produced bio-diesel in the distillation of bio-oil, a product was achieved very similar to the refinery diesel from the distillation perspective. Actually, the main reason of proximity between the properties of diesel and bio-diesel (as shown in Table II) is the similarity of their distillation curve, which means similar distribution of molecular weight.

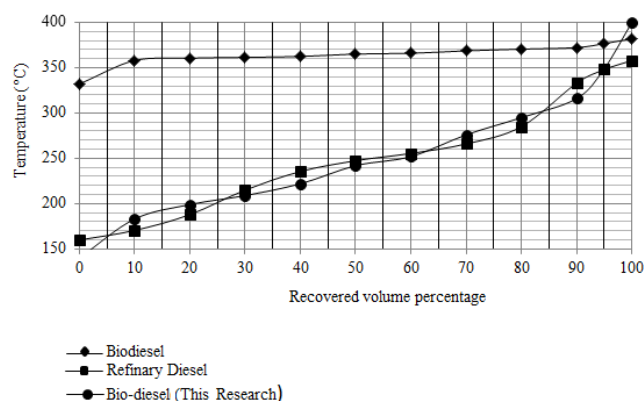


Fig. 2 Distillation Curves of castor oil biodiesel, refinery diesel and bio-diesel

Analyzed properties of the produced bio-diesel show that thermal cracking of the biodiesel is a viable process as these properties were approved by the criteria of ASTM D975. Moreover, most of the examined properties of the produced bio-diesel show improvement, in comparison with biodiesel, through this process.

The important drawback of the FAME based biodiesel is its high cold flow properties meaning that this fuel is not proper for cold weather conditions. Cloud point and pour point are mostly above zero. Thermal cracking of biodiesel improves its cold flow properties by decreasing them considerably, which might eliminate the use of additives. However, castor biodiesel poses low cold flow properties but even though they have shown great improvement in these experiments.

Unlike its worthy cold flow properties, castor biodiesel poses very poor Kinematic viscosity. Kinematic viscosity is not a downside of biodiesel for most of the oils it is produced. This process could decrease the high kinematic viscosity of the castor biodiesel sufficiently so that the kinematic viscosity of the castor bio-diesel is approved by the criteria of ASTM D975.

Heating value (HG) is another fuel property indicating the economic efficiency of diesel fuel. Heating value of the biodiesel is lower than the petrol based diesel, which is another shortage of the biodiesel as a renewable fuel. As shown in Table II, high heating value of castor biodiesel is improved noticeably during the thermal cracking, which could be comparative with the refinery diesel.

High flash point means burning issues of the fuel and very low flash point means less safety of fuel storage. In this process, flash point is decreased near to the borderline of standard amount.

High cetane number is one of the advantages of biodiesel, which is much higher than that of refinery diesel. In this process, cetane number has decreased. Cetane index of the bio-diesel produced by thermal cracking of biodiesel is still sufficient, as it is more than the standard amount although it is decreased a deal.

B. Properties of the Bio-Diesel

The produced bio-diesel samples obtained from the thermal cracking/distillation units were characterized by their density, kinematic viscosity, cold flow properties and cetane index (Table III). Statistical studies indicate that both reaction parameters have significant influence on the properties of the purified bio-diesels while their binary interactions have minor effect.

Density, kinematic viscosity and cetane index values were fitted with quadratic equations while cold flow properties were fitted with linear ones. Mentioned properties change through the experimental factors and studying the response surfaces indicate the variations.

These properties relate to the molecular structure of the samples and differ by changing the experimental factors. Factors important in molecular structure are chain length, degree of saturation, configuration of double bonds, branching, and aromatic content.

TABLE II
COMPARISON BETWEEN THE PROPERTIES OF CASTOR OIL BIODIESEL, REFINERY DIESEL AND BIO-DIESEL

Property	ASTM Test Method	Biodiesel (Castor)	Refinery diesel (No.2) (ASTM D975)	Bio-Diesel (This Research)
High Heating Value (Mj/Kg)	D4868	37.9	-	44.240
Flash Point (°C), Min	D 93	191	52	55
Physical Distillation Temperature (°C) (90% Vol. recovered)				
Min	D86	372	282	330
Max			338	
Kinematic Viscosity (mm ² /sec) at 40 °C				
Min	D445	16	1.9	2.2
Max			4.1	
Cetane Index, Min	D976	60	40	42
Density (Kg/m ³) at 15 °C	D4052	926	-	871
Cloud Point	D2500	-21	-	-29
Pour Point	D97	-37	-	-45

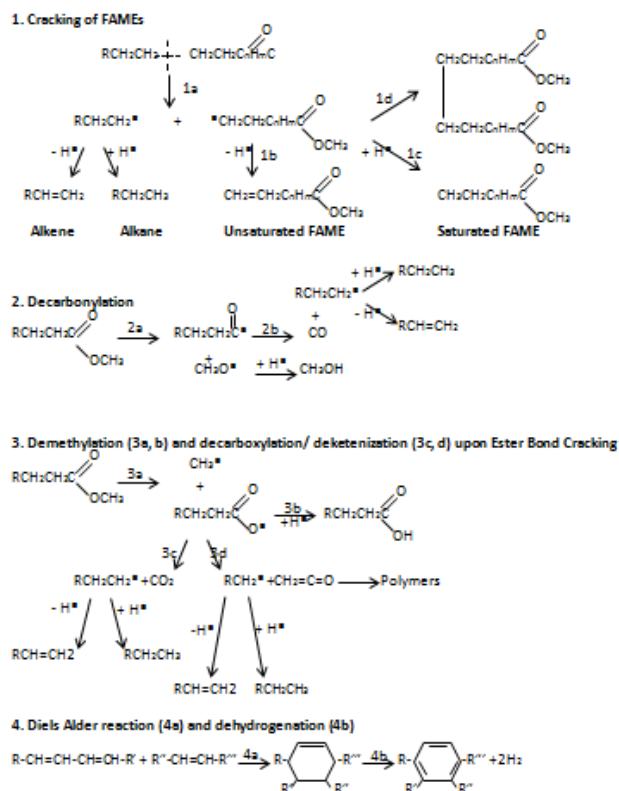


Fig. 3 Thermal decomposition reactions of biodiesel

Cracking becomes severe by increasing the temperature of the reaction and/or residence time. In these conditions, more cleavage of chemical bonds and more shortening of the chain length happen. Therefore, by increasing the temperature of the reaction and/or residence time lighter molecules are expected.

Impact of the thermal cracking parameters on saturation degree is not found in the literature, however comparison between feed and products imply that increasing the temperature of the reaction and/or residence time could increase the saturation degree of the products [9], [16].

TABLE III
PROPERTIES OF BIO-DIESEL SAMPLES

Run Number	Density @20°C (Kg/m ³)	Kinematic Viscosity @40°C (cst)	Cloud Point (°C)	Pour Point (°C)	Cetane Index
1	866.8	2.1	-33	-36	42.32
2	862	1.82	-42	-45	39.72
3	872	2.19	-18	-30	42.03
4	867	1.93	-33	-36	41.32
5	869.2	2.48	-27	-33	42.49
6	865	2.03	-36	-39	40.19
7	866	1.95	-39	-39	40.89
8	870.2	2.73	-21	-30	41.82
Center Point	868.4	2.41	-33	-36	41.06

Density of the hydrocarbons increases with chain length (number of carbon atoms) which happens by increasing the

temperature and/or residence time of cracking. According to the response surface, density of bio-diesel decreases with increasing the temperature and/or residence time.

Viscosity of the hydrocarbons increases with chain length (number of carbon atoms) and degree of saturation. Moreover, factors like double bond configuration affect viscosity (cis double bond configuration giving a lower viscosity than trans) whereas double bond position affects viscosity less[17]. According to the response surface, kinematic viscosity of the bio-diesel decreases with increasing the temperature and/or residence time for generation of shorter chain molecules. Moreover, variation of the viscosity in the lower residence time (near to 40g/hr) is negligible.

Biodiesel performance at cold weather is an important quality criterion. The key parameters for low temperature fuel applicability are cloud point and pour points. ASTM D975 does not include minimum values for them but the values should be reported (Table II). Lower cloud point and pour point result better cold flow properties.

Cloud point refers to the temperature below which wax in diesel or biowax in biodiesel forms a cloudy appearance. Pour point refers to the temperature at which the fuel becomes semi solid and loses its flow characteristics.

One of the major issues for biodiesel usage is poor cold flow properties, indicated by relatively high cloud points and pour points. Unsaturated fatty compounds have significantly lower melting points than saturated fatty compounds. Thus, biodiesel fuels derived from fats or oils with minor amounts of unsaturated fatty compounds will display higher CPs and PPs [18]. Also, cloud point decreases with branching and lower chain length [19].

Cold flow properties of bio-diesel decreases with increasing the temperature and/or residence time as shrinkage of chain and branching increases. Reversely, in high temperature and/or high residence time, degree of saturation increases that leads to higher cold flow properties but increase of saturation degree is negligible.

Cetane number is a measure of the ignition delay of a diesel fuel. A high cetane number helps to ensure short interval between fuel injection and its burning. Cetane number is mostly significant in low temperature starting and even combustion[20]. The Cetane Index is useful for estimating cetane number when a test engine is not accessible for determining this property directly.

Cetane number relates to the structure of the molecules and it increases with increasing the chainlength, increasing saturation, and decreasing branching. Aromatic compounds have low CNs[18]. Therefore, CN is expected to decrease by increasing the temperature and/or residence time of cracking.

As expected and according to the response surface, CI of bio-diesel decreases with increasing the temperature and/or residence time as the shrinkage of chain chances more and chain length decreases. Indeed, at high temperature and/or high residence time, more aromatic is produced leading to lower CN.

IV. CONCLUSION

Through this study, thermal cracking approach was recognized an efficient method to improve the properties of biodiesel. Temperature of the reaction and feed flowrate were studied as two main process parameters in this investigation, which had significant impact on the yields and properties of the products. Noticeable amount of material loss exists in this process; therefore, additional studies are required for economical investigation of this technology.

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