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BIODIESEL PRODUCTION FROM CORN OIL BY TRANSESTERIFICATION PROCESS

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There is much political demand and economic pressure to convert agricultural surpluses into material, such as motor fuel, in which the world is deficient. Transport industry is primary consumer of crude oil. Due to scarcity of known petroleum reserves, the possible alternative fuel for use in present engine technology is biofuels. Europe, USA and Brazil are successfully using biofuels. Biofuels causes less environmental pollution as compared to normal petro fuels. As a fuel, ethanol (gasohol) is used in internal combustion engine while methyester (Biodiesel) is used in diesel engines with same or better performance as compared to petro fuels. Corn is very valuable crop with numerous industrial applications, and is used in more than 300 modern industries, including the manufacture of textiles, paper, adhesives, insecticides, paints, soaps, explosives and many more. Presently the biggest source of ethanol production is from corn (produced by USA). Edible oil can also be extracted from corn which is normally used for cooking and it can be used for biodiesel production. Many countries are experimenting on fats and oil to get feasible data for production of biodiesel. Presently USA prefer to use soybean oil as raw material for commercial production of biodiesel while in Europe rapeseed oil is preferred, so therefore, it depends upon the availability of raw material in particular area and may change from location to location. In Pakistan we started with corn oil to produce biodiesel by transesterification method. In present study different design parameters such as effect of temperature, catalyst concentration, molar ratio, and Stirrer speed were founded for better conversion of neat and used corn oil into biodiesel. The optimum parameters proposed for neat corn oil are 0.5% of catalyst based on weight of corn oil, temperature between 50^{o}C to 60^{o}C, reaction time 15 minutes, molar ratio of 6:1 and speed of stirrer 155 rpm. In case of used corn oil high catalyst amount was used which was 0.7% based on the weight of oil. Fuel testing results of corn biodiesel was comparable with normal petro diesel fuel.

Keywords: Corn oil, Methanol, Free fatty acid, Transesterification

1. Introduction

The demand of petroleum crude oil is increasing with the passage of time due to a rapid increase in civilization and industrialization. In 2004 the world needed 83 million barrels per day which is expected to increase to 118 million barrel per day in 2030 [1]. This rapid growth will be due to heavy economical and industrial activities in Asian countries. OPEC producers are expected to provide more than one-half of the additional production in 2015 and more than two thirds in 2030. According to Oil & Gas Journal, World Oil, and BP's Statistical Review of World Energy, Non-OPEC production in 2030 is projected to be 12 million barrels per day higher than in 2004, representing a 35 percent increase in total world production over the 2004 total. The two main consumers of petroleum crude oil are transport sector and petro based chemicals industries [2]. For the present transport sector, the only possible reciprocal fuel is Biofuels, produced from agricultural products.

The economy of Pakistan is growing and its need for petroleum crude oil and its products is also increasing. Presently, Pakistan has enough resources of natural gas; however it imports petroleum crude oil to fulfill its requirements. During first 11 months of 2006, Pakistan had consumed approximately 350 thousand barrels of oil and various petroleum products, of which, more than 80 percent was imported [3]. Transport sector is the biggest consumer of oil which accounts for about 48% followed by power sector; 36% and the remainder being shared by industrial and residential sectors [3]. Transport sector comprises of both private and commercial vehicles. The cost of transport fuel is continuously increasing due to rising cost of petroleum crude oil compelling the Government of Pakistan to increase the cost of both petrol and diesel fuel, which is badly affecting the life of common man [4].

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Table 1. ASTM test methods and limits for fuel prosperities[a].

Property	Unit	ASTM method	Limits
Kinematic viscosity (v) at 40° C	mm^2/s	D 445	1.9-4.1
Distillation temperature at 90 vol% recovered	°C	D 86	282-338
Cloud point (CP)	°C	D 2500	-b
Pour point(PP)	°C	D 97	-c
Flash point (PP)	°C	D 93	≥ 52
Water and sediment	vol%	D 2709	≤ 0.05
Carbon residue at 10% residue	wt%	D 524	≤ 0.35
Ash	wt%	D 482	≤ 0.01
Sulfur	wt%	D 2622	≤ 0.05
Copper strip corrosion rating 3 h at 50°C	-	D 130	No 3 (max)
Cetane number	-	D 613	≥ 40

[a]Source: Reference 13 and 14 for information on low-sulfur (500ppm) No.2 diesel fuel(DF2).ASTM, American Society for Testing and Materials.

[b]CP not specified by ASTM D 975. In general, CP may be used to estimate low operating temperature for fuels not treated with cold flow improver additives. When additives are present, alternative methods D 4539 or D 6731 should be employed.

[c]PP not specified by ASTM D 975. PP is generally 4-6°C below CP according to liljedahi et al. (105).

Industrial civilization, economic growth and life style of the developed world are dependent on inexpensive oil and gas. The energy and products from cheap oil have made possible the industrial revolution spanning over the last century and the close ties amongst indigenous cultures. Affordable food production needs inexpensive natural gas and oil inputs for: fertilizers, pesticides, industrial machinery, planting, cultivating, harvesting, processing, packaging, transportation and marketing. Association for the study of peak oil provides a statistical finding of depletion projections. Big oil based multinational companies don't address the depletion issue seriously [5]. Presently auto industry, which is totally dependent on crude oil and gas fuel, is introducing the technology shifts, such as hydrogen fuel cells etc. They are also considering the uses of biofuels as a possible substitute for present petro based fuels. Alkyl ester (Biodiesel) and ethanol (gasohol) can be efficiently used in present day engines and causes less environmental pollution as compared to petro fuel.

According to many researches, there are considerable and valuable advantages of using Biofuels. As Industrial crops are carbon nutrient, energy is used in the form of fertilizer, insecticides, agriculture machinery, and transportation and thus increases pollutant concentration. Inspite of this, overall life cycle analysis proves a 50% to 60% decrease of carbon emissions [6]. It enhances economic activity by engaging a large number of populations in their fields and thus improves the standard of living.

Biodiesel is obtained from the chemical reaction of vegetable oil or animal fats with alcohol in the presence of catalyst and the reaction is termed as Transestreification. Triglyceride molecules of vegetable oil and animal fats have different fatty acid chains which are attached to the glycerol backbone, and are responsible for specific physical and chemical properties. The use of vegetable oil or animal fats in diesel engine is not a new concept. Rudolf Diesel, inventor of diesel engine described the use of peanut oil as a fuel in Paris exhibition in 1900. The working performance of vegetable oil fuel and petro diesel fuel was same. According to Diesel, several other vegetable oils, such as castor oil and animal oil were tested in St.Petersburg which yielded satisfactory results [7, 8]. Brazil used cotton seed oil as fuel in World War II and prohibited its export [9]. China produced diesel fuel, lubricating oil, gasoline, and kerosene by cracking of animal fats and vegetable oil [10, 11]. The term used for vegetable oil based fuel, Biodiesel, first appeared in a Chinese paper published in 1988 [12]. Some other applications of vegetable oil include lubricants oil, power generation, and as a heating source have been discussed in earlier publication [13, 14].

The suitability of alternative fuel for diesel engines is tested by ASTM D 975 [15, 16]. The standard fuel properties and their range is given in Table 1. Among the most important fuel properties are, viscosity at 40°C, distillation temperature, cloud point, pour point, flash point, water and sediment, carbon residue ash, sulfur, copper strip corrosion residue, and cetane number[15,16].

Most of the tests on engine performance and durability don't match with standard by using neat vegetable oil and vegetable oil/No.2 petro diesel blends and led to incomplete combustion, nozzle coking, engine deposits, ring sticking, and contamination of crank case [17-20]. High viscosity of vegetable oil is one of the main reasons for pure durability problems which cause pure atomization [21]. Vegetable oil can be used as diesel engine fuel by lowering its viscosity value [21, 22]. The viscosity can be decreased by a number of ways such as: (1) Dilution in petrodiesel; (ii) conversion to Biodiesel (Transesterification) (iii) Pyrolysis and (iv) Micro emulsification.

Dilution of vegetable oil didn't work well in the modern direct injection engine and yielded similar problems as given by using neat vegetable oil. One study of dilution of rapeseed oil with petrodiesel showed that only a 30% blend of rape seed oil with diesel oil was possible to ensure adequate working of engine, however on opening of engine coking and sticking ring problems were noted [23]. Pyrolysis or cracking techniques for lowering viscosity also didn't flourish well due to high operating cost and process involved the cleavage of chemical bonds to smaller molecule [24]. Several researches such as, cracking of used cottonseed oil in presence of a catalyst Na_2CO_3 yielded alkanes of range C_8-C_{20} with comparable standard of diesel fuel properties [25]. Microemulsion and co-solvent blend is also another method of reducing viscosity of vegetable oil. Low molecular weight alcohols such as methanol and ethanol are generally mixed with vegetable oil to form hybrid fuel. Alcohols are normally less soluble in vegetable oil and thus require surfactant to increase the solubility in vegetable oil which then decreases overall viscosity [18]. Due to addition of surfactants compound, two different phases forms single phase and there is no need of remixing [26]. Finally it is generally mixed with co solvent (normally Petro diesel) to be used in diesel engine. The main drawback of using this technique is that in many cases it lowers the flash point and thus makes it a more unsafe fuel [27].

The most common method used for lowering the viscosity of vegetable oil is Transesterification. Biodiesel term is only used for product produce by Transesterification process, normally methyl ester. Methanol is normally used because it is cheaper than other alcohols, however in some countries like Brazil, ethanol is cheaper than methanol and that's why they prefer to use ethanol. In industry, Transesterification reaction can precede in the presence of acid or base catalyst, however base catalyst is more rapid process as compared to acid catalysis [28-30]. Beside catalyst, some other parameters such as molar ratio of alcohol to vegetable oil, temperature, reaction time, refinement of vegetable oil, and presence of free fatty acids may affect the product yield and its rate [29]. In principle, Transesterification reaction is reversible, however after reaction biodiesel and glycerol don't mix with each other and may yield to 97% [28].

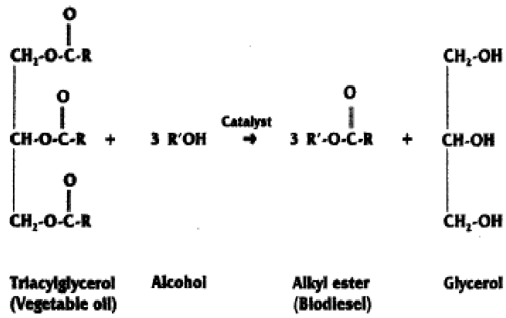

Figure 1. Transesterification Reaction.

Any vegetable and animal fat oil may be used for Biodiesel production but characterization may be simple on the base of free fatty acids. If vegetable oil/ animal fats have high concentration of free fatty acid, then normal alkali catalyst process can not be used because of soap formation. It is necessary to esterify or eliminate the free fatty acid before converting it into Biodiesel. Current Biodiesel quality imposes strict limits on the level of free fatty acid [31, 32]. Any vegetable oil/animal fats having free fatty acid concentration upto 4% can be esterified by base catalyst, but if free fatty acid concentration is high than alternative method should be used. Two approaches are used in these cases that is, free fatty acid are converted into soaps with alkali and thus decreases the free fatty acid concentration and second is a two step processes. In the two step approach, free fatty acids are first esterified (alkyl ester) in the presence of acid catalyst and then shifted to alkali Transesterification reactor [33].

Pakistan is an agriculture country and agriculture provides livelihood to two-thirds of the country's population living in rural areas, contributes 22 per cent to GDP, 60 per cent to exports and 45 per cent to employment of the labour force [34]. Two commodities mainly rice and cotton is the exports [34]. It is, however, unfortunate that despite having rich lands, Pakistan which essentially has an identity of an agriculture based economy has to rely on imports for edible oil, wheat and milk [34]. Locally produced edible oil contributes only 32%, however total amount required is approximately 1.55 million tones [35]. The main source of local edible oil production is cotton seed. Cotton, primarily grown, for its fiber, contributes about 75 percent towards the total domestic edible oil production and thus is an important oil seed crop in Pakistan [34]. Rapeseed-mustard crops are grown on a large area, contribute on an average, about 21 percent in the edible oil production However, its oil is not used in the manufacture of vegetable ghee (hydrogenated vegetable oil in semi-solid form) as it contains high levels of erucic acid and traces of sulphur compounds (glucosinolates). Its oil is mostly used in pickles, deep frying, anointing body, as hair oil etc [34]. It is today's need to introduce new edible oil crops which may increase its share for local edible oil consumption and may be used for fuel purposes. A comparison of indigenously produced edible oil with imported oil is shown in Table 2 [34].

Table 2. Domestic production, import and value of edible oil.

Year	Domestic Production (000 tons)	Import (000 tons)	Value of import (Rs. Billion)
1999-00	607	1091	21.4
2000-01	642	1149	19.04
2001-02	646	1197	24.03
2002-03	665	1281	39.29
2003-04	678	1361	37.91
2004-05	842	1605	44.98

Corn processing industry is one of the biggest agro based industries and originally used for extraction of starch through wet milling process. Due to this high expansion and utilization, corn oil which was first considered byproduct is now a full edible oil source. Corn refineries have invested in research and development which resulted in the production of high quality edible oil. This valuable crop, is usually used in production of ethanol, animal feed, corn sweeteners, edible oil, and starch is extracted for food and industrial uses: paper, textiles, adhesives, plastics, baked goods, condiments, candies, soups and mixes [36]. The approximate quantity of ethanol and corn oil produce per hector are 3000 liters/hector and 172 liter/hector respectively [37]. Comparisons of different oils and their ester characteristics are described in Table 3 representing acceptable cetane number for diesel engines [38].

2. Experimental Procedure

Any vegetable oil and animal fats and many other materials such as used frying oil may be converted into biodiesel production; however, change in the reaction procedure have to be made due to the presence of free fatty acid. A molecule of triglycerides contains glycerol backbone which is normally known as bonded glycerol to which different fatty acid chains is attached. Free fatty acids may be disconnected from glycerol backbone due to presence of water. It is proved by a literature that with a low concentration of free fatty acids, i.e. upto 4 % can be transesterified by alkali catalyst for production of Biodiesel [39].

Batch and continuous flow reactors are in common practice depending upon the quantity or availability of raw material. The main purpose of experiments was to find out the effect of different operating parameters on the rate of conversion of both neat and used corn oil. Neat corn oil and used corn oil were converted to Biodiesel. Neat corn oil was obtained from local Peshawar University general store. Neat corn oil was cooked for nine (9) hours which increased free fatty acid concentration to approximately 1%. Sodium hydroxide was used as a catalyst. Methanol, a raw material for biodiesel production was of Merck (Germany, Darmstadt) Company. Different parameters for efficient conversion of corn oil were studied such as (1) Concentration effect of catalyst, (2) Temperature effect on yield, (3) effect of molar ratio of methanol to corn oil (4) time change effect on yield and (5) rotation speed of reactor.

The biodiesel production process converts the oils into alkyl esters, separating out Glycerin. The

Table 3. Oils and esters characteristics.

Type of oil	Melting Range in degree C			Iodine number Cetane number	
	Oil/Fat	Methyl ester	Ethyl ester		
Rapeseed oil, h. eruc.	5	0	-2	97 to 105	55
Rapeseed oil, i. eruc.	-5	-10	-12	110 to 115	58
Sunflower oil	-18	-12	-14	125 to 135	52
Olive oil	-12	-6	-8	77 to 94	60
Soybean oil	-12	-10	-12	125 to 140	53
Cotton seed oil	0	-5	-8	100 to 115	55
Corn oil	-5	-10	-12	115 to 124	53
Coconut oil	20 to 24	-9	-6	8 to 10	70
Palm kernel oil	20 to 26	-8	-8	12 to 18	70
Palm oil	30 to 38	14	10	44 to 58	65
Palm oleine	20 to 25	5	3	85 to 95	65
Palm oleine	20 to 25	5	3	85 to 95	65
Palm stearine	35 to 40	21	18	20 to 45	85
Tallow	35 to 40	16	12	50 to 60	75
Lard	32 to 36	14	10	60 to 70	65

Glycerin sinks to the bottom and the biodiesel floats to top and can be siphoned off. This process is called transesterification, which substitute's alcohol for the Glycerin in a chemical reaction, using NaOH as a catalyst.

Before starting transesterification reaction it is necessary to find the concentration of free fatty acid in sample because higher acid value may poison the catalyst. To find out concentration, 1 gm NaOH is dissolved in 1 liter of distilled water, so as to make 1 % NaOH solution. Every 1 ml of this solution will now contain 1/1000 of a gram of NaOH. With the help of titration, free fatty acid concentration is calculated in oil sample. If free fatty acid concentration is less than 4% then it is suitable for transesterification reaction.

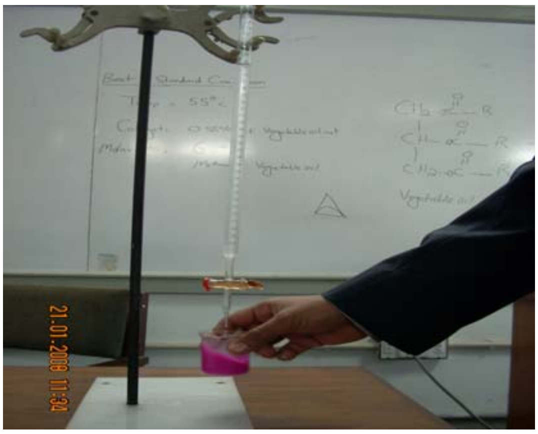

Figure 2. Titration of corn oil.

Vegetable oil initially heated above 45^{o}C so as to decrease the viscosity of vegetable oil and thus provides enough activity for alcohol. Equal amount of heat was supplied to bulk of reaction mixer. Approximately after 5 minutes the color of reaction mixtures changes and glycerol separates from corn oil and seemed on the inside surface of flask. After passing of 24 hours the two layers are separated and the glycerin can be easily separated from Biodiesel. Biodiesel must be freed from catalyst and excess methanol. 1 normal acidic solution was used for purification of Biodiesel. Excess catalyst, methanol, and soap dissolved in water and then separated as shown in figure.

Figure 3. Washing of Biodiesel.

500mls of corn oil was first heated according to required of degree of experiment. Methanol was used for transesterification reaction. Structure of methanol is very stable and forms an immiscible solution when added to corn oil. Alkali catalyst was used so that the electrophelic attack of methanol may be easier. A calculated amount of methanol reacted to corn oil and after passing some time, freed the glycerol from the parent corn oil molecule. Optimum reaction parameters were found in this experimentation. The main reaction is between corn oil and methanol in the presence of NaOH catalyst. Reaction can only proceed when the reactants have active face to face interaction with each other. By nature the methanol compound is stable and same is the case with corn oil (triglyceride). Methanol and corn oil are not easily miscible to each other. By adding a base, which is an electron pair donor helps the methanol to give better electrophelic attack and thus able to give methyester (Biodiesel). By nature the reaction is reversible, but due to great density difference of products the reaction can proceed to 100% in forward direction. As discussed earlier that the reaction is dependent on active interaction of compounds of Triglyceride and methanol, so providing the maximum opportunity for active interaction is in the best interest of forward reaction. The factors which can increase the contact of these compound molecules are molar ratio of methanol to corn oil, concentration of catalyst in reaction mixture, temperature of reaction mixture, and the time involved in reaction.

Many researchers found the effect of catalyst, temperature, molar ratio, and the time duration of reaction for better yield. A number of different vegetable oil has been used as discussed in introduction section. The R group as shown in above reaction (Fig 1) may have different fatty acid groups so therefore, the reaction parameter may vary from each other as discuss in earlier section. The different kinds of fatty acids (R) which can be in vegetable oil/animal fats are as under.

Palmitic: R = - $(CH_2)_{14}$ – CH_3 16 carbons, (including the one that R is attached to.) (16:0)

Stearic: R = - $(CH_2)_{16}$ – CH_3 18 carbons, 0 double bonds (18:0)

Oleic: R = - $(CH_2)_7$ CH=CH $(CH2)_7CH_3$ 18 carbons, 1 double bond (18:1)

Linoleic :R= -$(CH_2)_7$ CH=CH-CH_2-CH=CH(CH2) 4CH3 18 carbons, 2 double bonds (18:2)

Linolenic:R= -$(CH_2)_7$CH=CH-CH_2-CH=CH-CH2-CH = CH-CH2-CH3 18 carbons, 3 double bonds (18:3)

Corn oil triglycerides mainly consist of oleic and Linoleic fatty acid groups. For calculation purpose molecular weight of triglyceride molecule is 885 and molecular weight of methanol is 32.04. The conversion of triglyceride molecule is based on the weight of free glycerol, the higher the mass of free glycerol the higher will be the conversion of triglyceride molecule. The mass of free glycerol according to Stichometric equation can be obtained from main Stichometric equation.

(Free glycerol according to Stichometric equation)- (Difference of free glycerol and founded glycerol)*100/ (Free glycerol according to Stichometric equation) = % conversion of triglyceride molecule.

3. Results and Discussion for Neat and Used Corn Oil

NaOH was used as a catalyst for base catalyzed transesterification of corn oil for investigation of different parameters.

3.1 Effect of concentration of catalyst:

The effect of catalyst, NaOH concentration on the transesterification of corn oil was investigated. A number of publications show that by increasing the concentration of catalyst the conversion of triglyceride molecules increases, however a stage is reached when no further change will be observed. To find out the effect of catalyst change, the other parameters were fixed as done in previous researches. The calculated concentration varied between 0.3 to 0.6 % (based on the weight of corn oil). The reaction conditions during the whole process were fixed at reaction time 15 minutes, molar ratio of methanol to oil at 6:1 and the revolution speed 155 rpm.

It is found that increasing the concentration of catalyst increases the conversion of corn oil into methyl ester and glycerol. A linear increase was observed when concentration of catalyst increased from 0.3% to 0.5%; however beyond 0.5% conversion remained same upto the 0.6% as shown in Fig 4. It was also found that by increasing the concentration of catalyst beyond 0.5% increases the soap formation and thus large amount of water is required for washing step.

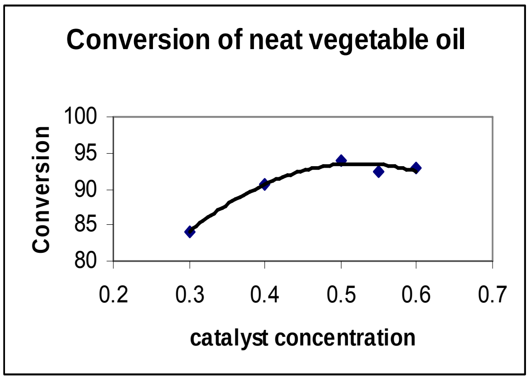

Figure 4. Effect of catalyst concentration on conversion of neat corn oil.

Used corn oil contains free fatty acids which may poison the catalyst. Therefore, some extra amount of catalyst is required for better conversion of corn oil into Biodiesel. In contrast of neat vegetable oil, 0.70 % (based on the weight of raw oil) of catalyst was found more appropriate as shown in Fig. 5.

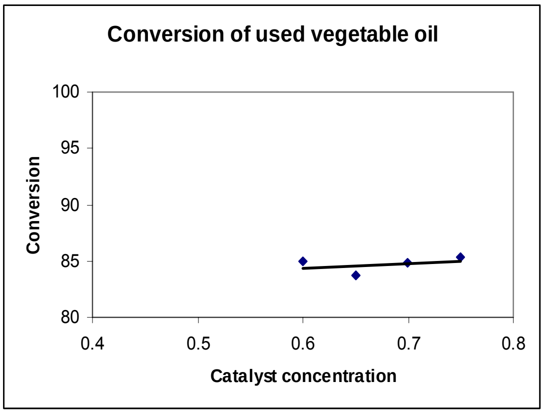

Figure 5. Effect of catalyst on conversion of used corn oil.

These results agree with those obtained by other authors. Nye et al. and Tomasevic and Siler-Marinkovic, in a process of transesterification of used frying oils with different alcohols also concluded that potassium hydroxide was the best catalyst [40, 41]. Zhang et al. reported that alkali-catalyzed process is sensitive to water [41]. The presence of water, under alkaline conditions may cause ester saponification.

3.2 Effect of molar ratio

The alcohol to vegetable oil molar ratio is one of the most important factors that can affect the yield of esters. Other parameters such as catalyst concentration effect, temperature effect, time duration and stirrer speed effect has little observable affect on conversion of corn oil. The catalyst concentration and reaction time as optimized in the previous section were adopted. The yield of methyl esters at different alcohol to vegetable oil molar ratio as 3:1, 4:1, 5:1, and 6:1 were observed. Maximum conversion of corn oil was obtained when having molar ratio 6:1. The higher molar ratio than the Stichometric value results in higher rate of ester formation. More over, it was observed that at higher molar ratio, a longer time was required for the separation stage because separation of ester layer from the glycerol was difficult.

Both neat and used corn oil with high molar ratio (6:1) converted efficiently to methyester as shown in Figs. 6 and 7. A linear increase in the methyester formation was observed when using high molar ratio of methanol to corn oil.

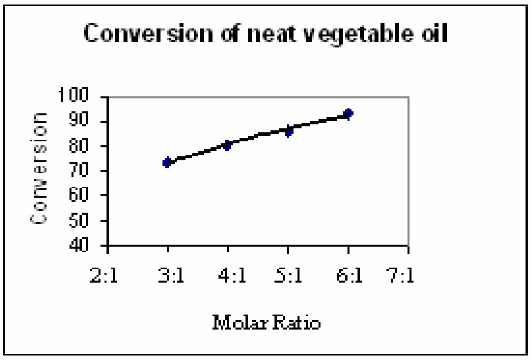

Figure 6. Effect of molar ratio on conversion of neat corn oil.

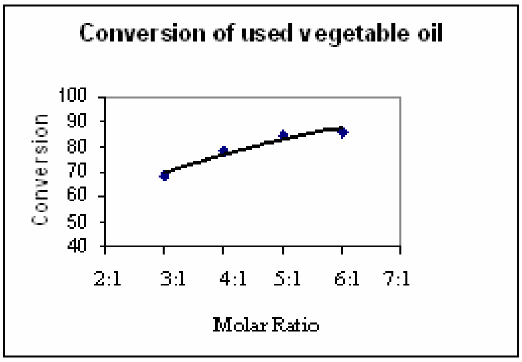

Figure 7. Effect of molar ratio on conversion of used corn oil.

Our results are in line with the reports of Zhang et al., Freedman et al. and Boocock et al [42-44]. Meher et al. and usta obtained high yields of esters utilizing the molar relation of 6:1 during the Methanolysis of P. pinnata and tobacco seed oil, respectively [45, 46].

3.3 *Effect of reaction temperature*

The effect of reaction temperatures, experimental trial were carried out at temperature of 50°C, 55°C, 60°C, and 65°C. In all experiments, a methanol/oil molar ratio of 6:1, 0.5%, and 0.7% of NaOH (as catalyst) were used (the optimal condition achieved in the previous section). Very little change was observed in the yield of ester. The time duration reaction was 15 minutes. In both neat and used corn oil the observe conversion was same as shown in Figs. 8 and 9.

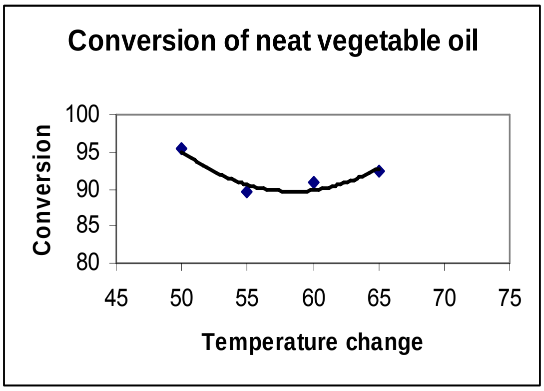

Figure 8. Effect of temperature change on conversion of neat corn oil.

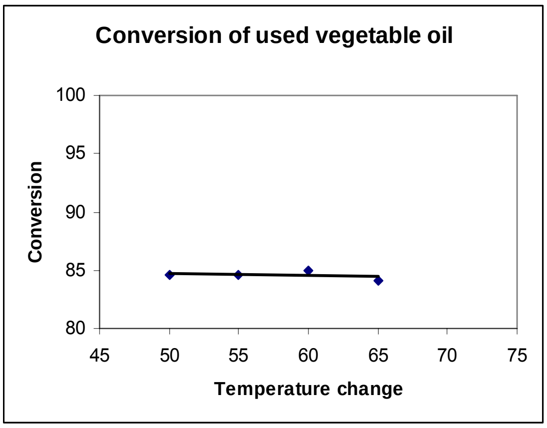

Figure 9. Effect of temperature change on conversion of used corn oil.

Karaosmanoglu et al. and Encinar et al. also investigated similar trends during the optimization of transesterification for production of biodiesel using rapeseed oil and Cynara cardunculus oil, respectively [47, 48].

3.4 *Effect of reaction time*

In present experimentation catalyst was first dissolved in methanol and after fully dissolving the catalyst it is added to corn oil. Almost 25 to 35 minutes are required to dissolve catalyst in methanol and then it is added into reaction mixture. In reactor, Just after 5 minutes clear viscous glycerol was observed at the surface of transparent round flask reactor. By nature reaction is reversible, but due to formation of two different density phases higher yield of biodiesel can be obtained. Experiments show that higher conversion of corn oil is obtained when the reaction is allowed for 15 minutes. Both neat and used oil produced same type of data as shown in Figs 10 and 11. Similar results are observed by A.Srivastava and R.Prasad and F.Ma and Hanna [49, 50].

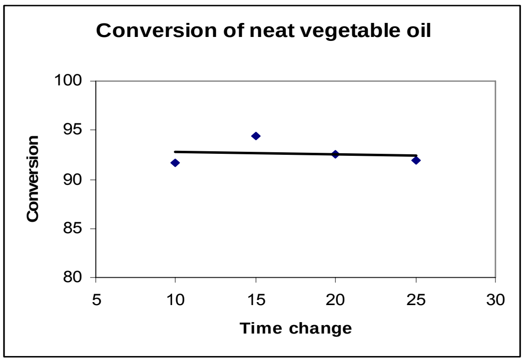

Figure 10. Effect of time on conversion of neat corn oil.

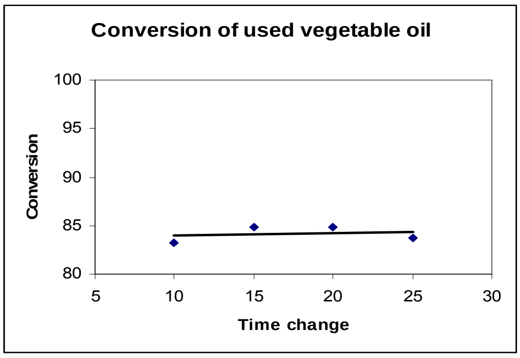

Figure 11. Effect of time on conversion of used corn oil.

3.5. Effect of rotation speed

The mixing intensity appears to be of particular importance for the transesterification process. It increases the intact area between oil, potassium hydroxide, and methanol solution. Mixing facilitates the initiation of the reaction. Without mixing, the reaction occurred only at the interface of the two layers and considered too slow to be feasible. In the present experiment, Methanolysis was conducted at different stirring speed such as 155, 165, 175 and 185 revolutions per minute (rpm). The reaction results showed small variance in conversion of corn oil. For neat oil, a methanol/oil molar ratio of 6:1 and 0.5% of NaOH, and temperature 55^{o}C (as catalyst) were used (the optimal condition achieved in the previous section) and for used oil catalyst concentration used was 0.7% based on weight of oil. It was observed that the reaction of Methanolysis for both neat and used corn oil was practically giving high yield at stirrer speed of 155 rpm as shown in Figs.12 and 13. These results are in accordance with Ma et al. and Peterson et al., who studied the effect of agitation on the transesterification of vegetable oil and concluded that higher agitation promoted the homogenization of the reactants and thus lead to higher yields [51].

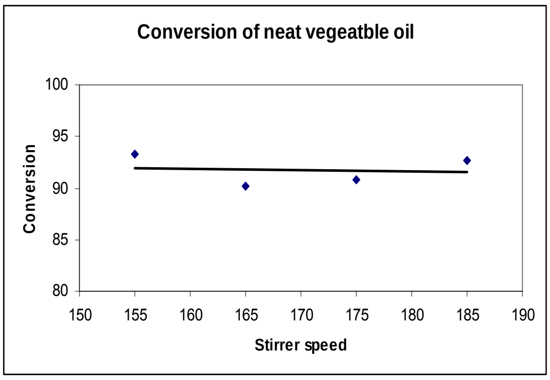

Figure 12. Effect of stirrer speed on conversion of neat corn oil.

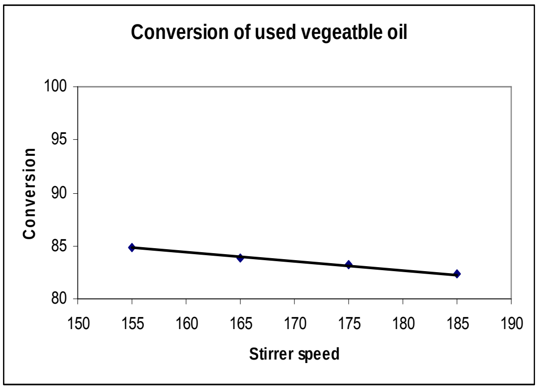

Figure 13. Effect of stirrer speed on conversion of used corn oil.

4. Analysis of Produced Biodiesel

The fuel properties of Biodiesel and mineral diesel were determined using standard test procedure. The Calorific value was calculated in Fuel and Furnace Laboratory of Chemical Engineering Department by using auto bomb calorimeter, shimadzoo Japan CA-4RT. Calorific value is the measure of energy content of fuel and finds the suitability of alternative fuel to normal petro diesel. The value found was little less because of presence of bonded oxygen in molecular structure, which is confirmed by elemental analysis.

The cetane number is a measure of the ignition performance of a diesel fuel obtained by comparing it to reference fuels in a standardized engine test. Cetane for diesel engines is analogous to the octane rating in a spark ignition engine; it is a measure of how easily the fuel will ignite in the engine. Cetane number is calculated with help of formula developed API. The calculated value of cetane number of Biodiesel was 49 and thus fulfills the standard value.

Biodiesel fuel can't be fully freed from methanol thus it lowers the flash point of fuel. By low flash point it means less safe fuel. In Europe the minimum flash point should be above than 101^{o}C while according to USA standard its minimum value should be greater than 130^{o}C. The flash point is defined as the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. This test, in part, is a measure of residual alcohol in the B100.

Table 4. Testing of biodiesel fuel properties.

Property	Test procedure	Standard values	Corn oil biodiesel
Cetane number	ASTM D613	47 minimum.	49
Kinematic Viscosity	ASTM D445	1.9-6.0 min2/sec.	5.9 mm²/s
Flash point	ASTM D93	130 °C minimum	212 °C
Specific gravity	ASTM D 1298	Not Required	0.887
Pour point	ASTM D97	0°C minimum	More cool then -16^{o}C
Cloud point	ASTN 2500	Report to customer	-2^{o}C
Sulphated ash	ASTM D 874	0.020% mass max	0.01
Copper strip corrosion	ASTM D130	No. 3 maximum	No. 2
Carbon residue	ASTM D189	0.050% mass maximum	0.03
Phosphorus	ASTM D4951	0.001% mass maximum	0.0002
Acid number	ASTM D 664	0.80 mg KOH/gm maximum	0.52
Calorific Value	ASTM D 240	44.8Mj/kg (Standard mineral Diesel)	35.4Mj/kg
Total Glycerine	ASTM D 6584	0.240% mass maximum	0.13

Most of fuel properties such as, Cetane number, flash point, and Kinematic viscosity were calculated in Hydrocarbon institute whose basic function is to check the quality of fuels in pump stations. The main diesel fuel properties, cetane number and calorific value were very much according to standard.

5 Conclusions

The study on the transesterification reaction conditions of corn oil indicated that the quantity of catalyst, molar ratio of methanol to oil, reaction temperature and reaction time were the main factors affecting the reaction.

Base catalyzed transesterification with NaOH as a catalyst was studied for the production of Biodiesel from corn oil. It is found out that the main factor which drastically increases the yield of Biodiesel is molar ratio of methanol to corn oil while other parameters are also needed for better efficiencies. The optimum parameters proposed for neat corn oil are 0.5% of catalyst based on weight of corn oil, temperature between 50 to 60^{o}C, reaction time 15 min, molar ratio of 6:1 and stirrer speed of 155 rpm. The only difference observed for used corn oil is use of high concentration of catalyst concentration based on the weight of vegetable oil. The proposed concentration for used oil is 0.7% based on the weight of corn oil.

Beside transesterification reaction, catalyst and methanol removal from biodiesel was also studied in detail. Transesterification reaction parameters control the yield of Biodiesel, whilst catalyst removal is also necessary and important to make Biodiesel fit for Diesel engines. It was found that with higher agitation in purification process may form emulsion and thus required more time and water in settling step, therefore degrades Biodiesel.

The viscosity of corn oil was substantially reduced after transesterification and its fuel properties were comparable to mineral diesel. These entire tests for the characterization of corn oil demonstrate that corn oil Biodiesel is potential substitute for diesel fuel in compression ignition engines.

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