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Acid Catalysis of Waste Cooking Oils for Biodiesel Production

I. V. Priya[1], S. V. A. R. Sastry[2]*, A. Sahoo[1]

[1] *Department of Chemical Engineering, National Institute of Technology Rourkela, India*
[2] *Department of Chemical Engineering, MVGR College of Engineering (Autonomous), Vizianagaram, Andhra Pradesh, India*

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A B S T R A C T

Sustainable energy source and pollution free environment is the immediate requirement of developing countries. Waste cooking oils of five different origins were considered in the present work for biodiesel production. Attempt was made to study the effect of process variables on acid-catalyzed oil transesterification. The various parameters such as catalyst amount, reaction temperature, reaction time, molar ratio of alcohol, and free fatty acids were analyzed to determine the optimum condition for biodiesel production. Food grade coconut, mustard, olive, peanut and soybean waste cooking oils were used to produce biodiesel. Attempt was made to develop mathematical expressions by correlating different input parameters and yield of biodiesel obtained with all the five oil samples. The experimental yield was also compared with those obtained from developed correlations. Good agreement among experimental and theoretical values was observed which implies that this study maybe considered as a base line for the development of an optimum biodiesel production plant.

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INTRODUCTION

In India, total primary energy consumption was nearly 0.72 Billion tons of oil equivalent in 2018, which is expected to rise up to 1.2 Billion tons of oil equivalent by 2035 [1]**.** In such a scenario, biodiesel utilization program seems to be a promising solution.

Biodiesel is produced by transesterification of oil or fat (lipid source). During transesterification process at mild operating conditions, generally a catalyst is involved as it speeds up the chemical reaction by lowering the amount of energy that is needed to complete the process [2]. Acid catalysts are found to be efficient in catalyzing the transesterification process. However, alkali-catalyzed reactions are characterized by high reaction rates under mild operating conditions [3]. The use of alkali metals in transesterification of low quality oils in the presence of free fatty acids is therefore recommended by many researchers [4]. Many researchers have focused on development of heterogeneous catalysts to simplify purification [5].

Nowadays, refined edible oils are very widely used as the primary raw material in the biodiesel industry [6]. The use of food-grade vegetable oil in transesterification often results in high purity biodiesel but limits its commercialization as production costs are high [7]. It has been reported that the cost of feedstock constitutes about 60-80% of the overall cost in the production process [8]. Every year, large amounts of waste oils are produced from restaurant waste, frying oils and trap grease, etc. which could be utilized for biodiesel production. The problem with processing waste cooking oils is that often these oils contain significant amounts of free fatty acids which cannot be converted to biodiesel using an alkaline catalyst. These free fatty acids react with the alkaline catalyst and forms soaps that inhibits the separation of the biodiesel, glycerin, and wash water [9,10]. Thus, an alternative way of utilizing these waste cooking oils is to make use of acid catalysts which might have greater tolerance for free fatty acids [11-14]. That is why it was thought to have a detailed study on this alternative way.

It is revealed from literature that production of biodiesel from waste cooking oils is possible by using acid catalysts [15,16]. It was thus felt to have knowledge on optimum process conditions with the waste cooking oil and acid catalyst route. Oils of five different origins were considered in the present work for biodiesel production. Different oils i.e., food grade coconut, mustard, olive, peanut and soybean oils were used in this work. The objective of this work was to study the effects of different parameters such as the catalyst amount, the reaction temperature, the reaction time, the molar ratio of alcohol and the presence of water and free fatty acids upon completion of acid-catalyzed transesterification process.

As there are large numbers of variables that affect the transesterification reaction, it is required to carry out a series of tests based on all possible combinations of the variables. A

* Corresponding Author Email: svarsastry@yahoo.com (Susarla V. A. R. Sastry)

standard condition is required to be established and the effect of each variable is needed to be studied.

MATERIALS AND METHODS

Cooking oils (CO's) which are rich in specific fatty acids were purchased from the local market. The oils were separately cooked over and over in order to make it waste cooking oil. The fatty acid compositions of WCO are shown in Table 1. Other chemicals i.e., methanol (99.9% pure), potassium hydroxide, benzene, ethanol, sulfuric acid (98%) and phenolphthalein of analytical grade were also procured.

Transesterification reaction was carried out in a 250 ml flat bottom triple neck flask which was placed in a heating mantel as shown in Figure 1. The WCO was preheated to the desired temperature (45, 50, 55 and 60^0C) before the addition of sulfuric acid catalyst and methanol. The reactions were carried out by varying different parameters such as catalyst concentration (0.5 – 2.5 wt %), methanol to oil ratio (3:1 – 7:1 v/v) and reaction time (30 - 120 min). After the scheduled time, the reaction was stopped and the mixture was transferred into a separating funnel. The lower layer containing glycerol was drained off and the biodiesel rich phase was separated after water wash. The same procedure was repeated for all the 5 oil samples.

TABLE 1. Fatty acid composition for five different waste cooking oils

FA Composition (% mass)	Different Waste Cooking Oils				
	Coconut	Mustard	Olive	Peanut	Soybean
Capric (C10:0)	6-10	-	-	-	-
Lauric (C12:0)	44-52	-	-	-	-
Myristic (C14:0)	13-19	-	0.1-1.2	-	0.5
Palmitic (C16:0)	8-11	1.5-2.0	7-16	6-9	7-11
Stearic (C18:0)	1-3	0-0.4	1-3	3-6	2-6
Oleic (C18:1)	5-8	22-25	65-80	52-60	22-34
Linoleic (C18:2)	0-1	10-15	4-10	13-27	43-56
Linolenic (C18:3)	-	6-7	-	-	5-11
Arachidic (C20:0)	0-0.5	-	0.1-0.3	2-4	-
Any special FA	-	Erucic-47.0	-	-	-
Predominant FA	Lauric	Erucic	Oleic	Oleic	Linoleic
Fatty Acid content (% of oil wt.)	64	70.5	84	76	77.5

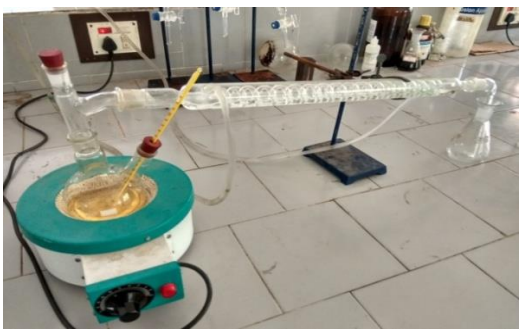

Figure 1. Experimental Setup for production of biodiesel

RESULTS AND DISCUSSIONS

The effect of different process parameters on the yield of biodiesel using acid catalyst were analyzed. Attempt was made to correlate all these input parameters i.e. amount of catalyst, temperature, time and molar ratio of alcohol to oil with the output parameter i.e. yield of biodiesel for five different oils.

Mathematical expressions for biodiesel yields

The following mathematical expressions were developed from the experimental results.

(i) For Coconut - waste cooking oil:

$$Biodiesel\ Yield = 0.003 \times [C^{0.290} \times T^{1.908} \times t^{0.334} \times M^{0.400}] \quad (1)$$

(ii) For Mustard - waste cooking oil:

$$Biodiesel\ Yield = 0.137 \times [C^{0.316} \times T^{0.809} \times t^{0.450} \times M^{0.492}] \quad (2)$$

(iii) For Olive - waste cooking oil:

$$Biodiesel\ Yield = 0.001 \times [C^{0.320} \times T^{2.223} \times t^{0.416} \times M^{0.513} \quad (3)$$

(iv) For Peanut - waste cooking oil:

$$Biodiesel\ Yield = 0.001 \times [C^{0.317} \times T^{2.255} \times t^{0.452} \times M^{0.545}] \quad (4)$$

(v) For Soybean - waste cooking oil:

$$Biodiesel\ Yield = 0.039 \times [C^{0.241} \times T^{1.395} \times t^{0.284} \times M^{0.352} \quad (5)$$

The comparison of exponents for different parameters affecting biodiesel yield are shown in Table 2. The experimental yield was also compared with those obtained from calculations through the developed correlations for different waste cooking oils are shown in Table 3.

Effect of catalyst concentrationn The amount of catalyst is found to affect the conversion of vegetable oil to biodiesel significantly with 6:1 molar ratio of alcohol to oil at 60^0C temperature and 90 min of reaction time. Five different catalyst amounts i.e., 0.5, 1.0, 1.5, 2.0, and 2.5% of sulfuric acid, were used in the present study. It is observed that the effect of catalyst concentration is more on yield of biodiesel for waste cooking oil with coconut and soybean sources. Mustard waste cooking oil is found to be less affected with catalyst concentration in comparison to others (Figure 2).

TABLE 2. Comparison of effects of parameters for five different waste cooking oils through developed correlations

S. No.	Waste cooking oil types	Overall coefficient, K	Catalyst concentration, n1	Temperatur, n2	Time n3	Molar ratio, n4	Avg. Yield %
1	Coconut	0.003	0.290	1.908	0.334	0.400	72.6009
2	Mustard	0.137	0.316	0.809	0.450	0.492	76.2409
3	Olive	0.001	0.320	2.223	0.416	0.513	63.9304
4	Peanut	0.001	0.317	2.255	0.452	0.545	66.9912
5	Soybean	0.039	0.241	1.395	0.284	0.352	84.5358

TABLE 3. Comparison of Biodiesel yields of experimentally observed and calculated values for different oils

S. No.	Waste Cooking Oils type	Acid Catalyzed process		Base Catalyzed process	
		Std. Deviation	Mean Deviation	Std. Deviation	Mean Deviation
1	Coconut	4.7246	10.7361	8.2480	3.0183
2	Mustard	2.9042	0.5104	3.3079	0.4699
3	Olive	4.0912	12.2688	3.1764	0.5806
4	Peanut	4.0606	11.8697	3.1531	0.4668
5	Soybean	1.6765	0.6961	2.0407	0.9829

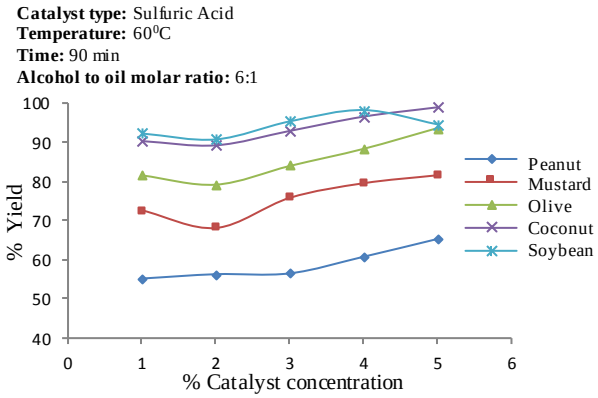

Figure 2. Biodiesel yield vs. Catalyst concentration

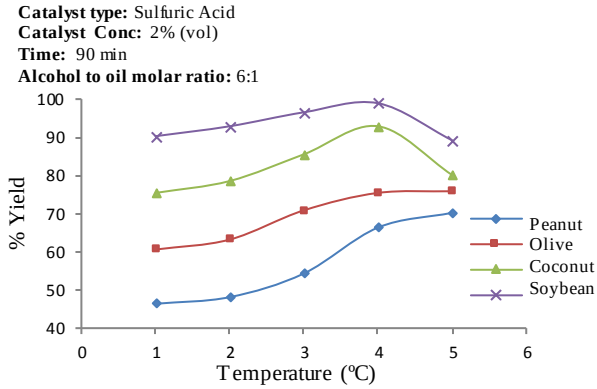

Figure 3. Biodiesel yield vs. Reaction temperature

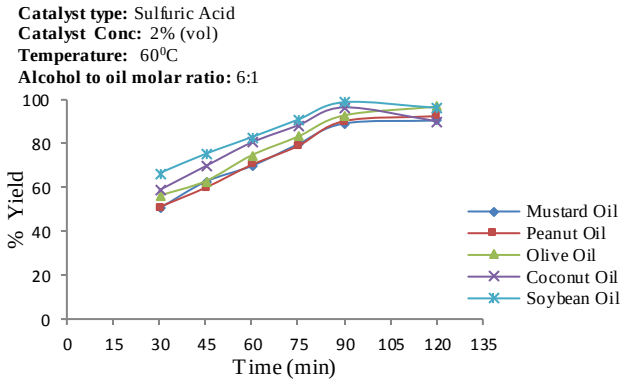

Figure 4. Biodiesel yield vs. Reaction time

Effect of reaction temperature

Reaction temperature is found to be another important factor that affects the conversion of waste cooking oil to biodiesel. It is observed from Table 3 that higher temperatures are required to fasten the reactions. In the present work four different temperatures i.e., 45, 50, 55 and 60°C, were considered. The highest temperature considered was 60°C, because it is close to the boiling point of methanol i.e., 65°C. It is observed that effect of temperature on the yield of biodiesel is more for soybean waste cooking oil than other waste cooking oils. Effect of temperature on biodiesel yield is lowest for mustard waste cooking oil (Figure 3). Reason may be due to Erucic acid content.

Effect of reaction time

Reaction time is another important parameter to be analyzed. Different reaction times i.e., 30, 45, 60, 75, 90 and 120 min, were considered in our study. The experiment in each case was conducted with 2% sulfuric acid concentration, 60°C reaction temperature and 6:1 molar ratio. It is evident from Figure 4 that all the waste cooking oils reacted in a similar fashion with variation in reaction time. Biodiesel conversions were negligible after 90 min of reaction time (Figure 4). However, 90 min was considered as the optimum duration for the study, but much more reaction times would give higher yields of biodiesel. Soybean and peanut waste cooking oils have relatively higher and lower yields.

Effect of alcohol to oil molar ratio

Alcohol to oil molar ratio is another parameter to investigate. Five different molar ratios i.e., 3:1, 4:1, 5:1, 6:1 and 7:1 were considered in the study. The experiment in each case was conducted with 2% sulfuric acid concentration, 60°C reaction temperature and 90 min reaction time. Biodiesel yields with 6:1 and 7:1 alcohol to oil molar ratios were very close to each other. From Figure 5, it is evident that coconut and soybean waste cooking oils have highest yields whereas mustard waste cooking oil had relatively lower yield.

Effect of acid and base catalysts on the yields of fame

The effects of different catalysts on percentage of yield of biodiesel for different types of esterified WCO are shown in Figure 6. The yield percentages for five different oils were

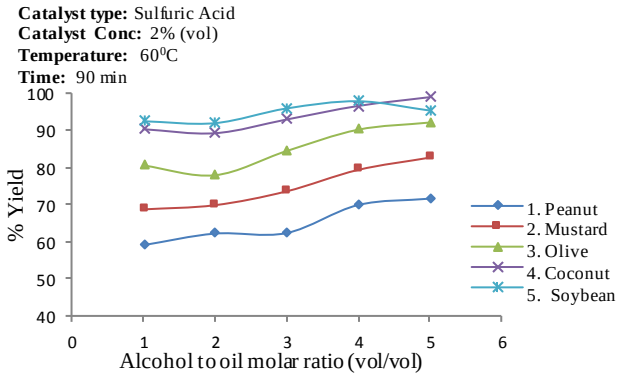

Figure 5. Biodiesel yield vs. Alcohol to oil molar ratio

calculated by maintaining the catalyst concentration, reaction temperature, reaction time and alcohol to oil molar ratio constant.

Soybean oil is found to give highest percentage of biodiesel yield i.e. 98.93% for acid catalyst and 97.32% for base catalyst followed by coconut oil, olive oil, peanut oil and the least yield was given by mustard oil with 89.21% for acid catalyst and 90.82% for base catalyst. Surprisingly, coconut oil is found to give almost same percentage of yield, nearly 96.54% for both acid and base catalysts. It is observed that for soybean and coconut waste cooking oils the biodiesel yields are more with acid catalyst compared to base catalyst (Figure 6).

Properties testing of biodiesel

Comparison of properties of waste cooking oil, biodiesel from waste cooking oil and commercial diesel fuel is shown in Table 4. The properties of biodiesel and diesel fuels, in general, show many similarities, and therefore, biodiesel is rated as a realistic fuel as an alternative to diesel. This is due to the fact that the conversion of waste cooking oil into methyl esters through the transesterification process approximately reduces the molecular weight to one third, reduces the viscosity by about one-seventh, reduces the flashpoint slightly and increases the volatility marginally, and reduces pour point considerably.

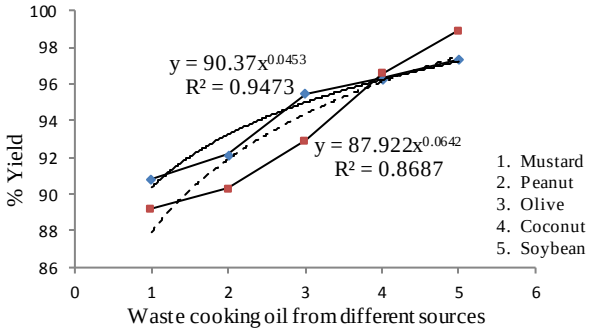

Figure 6. Comparison of biodiesel yields of different waste cooking oils through Acid and Base catalyzed transesterification

TABLE 4. Comparison of properties Waste cooking oil, Biodiesel and Diesel

S. No	Property	Waste cooking oil	Biodiesel from waste cooking oil	Diesel Fuel
1.	Kinematic Viscosity (mm^2/sec at 313K)	36.4	5.3	1.9 - 4.1
2.	Density (Kg/L, at 288K)	0.924	0.897	0.075 – 0.840
3.	Flash Point (K)	485	469	340 – 358
4.	Pour Point (K)	284	262	254 – 260
5.	Cetane number	49	54	40 – 46
6.	Ash content (%)	0.006	0.004	0.008 – 0.010
7.	Sulfur content (%)	0.09	0.06	0.35 – 0.55
8.	Carbon Residue (%)	0.46	0.33	0.35 – 0.40
9.	Water content (%)	0.42	0.04	0.02 – 0.05
10.	Higher Heating Value (MJ/kg)	41.40	42.65	45.62 – 46.48
11.	Free Fatty Acid (mg KOH/g oil)	1.32	0.10	-
12.	Iodine Value	141.5	-	-

CONCLUSIONS

Different waste cooking oils were used for analyzing effects of different parameters on yields of biodiesel obtained through transesterification process. The following conclusions may be drawn from the experimental observations.

The biodiesel formation was found to increase with increasing acid catalyst amount. The ester conversion is also found to be highly inhibited by the presence of water in waste cooking oil. Alcohols that have high boiling temperatures were found to increase biodiesel conversions. As the values of exponents i.e., n4 (Table 3) are less than one (0-1) indicates that the impact of molar ratio is low on biodiesel yields. Coconut and soybean waste cooking oils were found to be highly suitable for biodiesel production followed by olive, peanut and mustard waste cooking oils. The experimental values of yield were also compared with those obtained from the developed correlations which show good agreement with each other indicating the developed correlations to be satisfactory. Standard deviations and mean deviations were found to be in the range of 1.5 - 8.3 and 0.5 – 12.3 respectively, which implies that the developed correlations can be applied for designing an optimum biodiesel plant over a wide range of parameters. Soybean waste cooking oil has emerged as best waste cooking oil for biodiesel production as standard and mean deviation values were relatively low when compared to other oils.

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Persian Abstract

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چکیده

منبع انرژی پایدار وکنترل آلودگی محیط ، نیاز فوری کشورهای در حال توسعه است. روغن دور ریز پخت و پز از پنج منشا مختلف در کار حاضر برای تولید بیودیزل مورد توجه قرار گرفت. تلاش برای مطالعه اثر متغیرهای فرآیند بر روی ترانس اکسیداسیون روغن کاتالیز شده اسیدی انجام شد. پارامترهای مختلف مانند مقدار کاتالیزور، دمای واکنش، زمان واکنش، نسبت مولی الکل و اسیدهای چرب آزاد برای تعیین شرایط مطلوب تولید بیودیزل مورد بررسی قرار گرفت. برای تولید بیودیزل از روغن زیتون نارگیل، خردل، زیتون، بادام زمینی و روغن سویا استفاده گردید. تلاش برای ایجاد روابط ریاضی بوسیله همبستگی پارامترهای ورودی مختلف و عملکرد بیودیزل به دست آمده در تمامی نمونه های نفتی ساخته شده است. عملکرد آزمایشی نیز با مقادیر حاصل از همبستگی های توسعه یافته مقایسه شد. توافق خوب بین ارزشهای آزمایشی و نظری مشاهده شده است که این نشان می دهد که این مطالعه ممکن است به عنوان یک خط پایه برای توسعه یک کارخانه تولید بیودیزل بهینه باشد.