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A Comparative Study on Biodiesel Production from Waste Cooking Oil

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Abstract—*Use of fossil fuels at ever increasing rate has made it vulnerable to depletion. The economy of world depends on continuous supply of these fuels in absence of which it may collapse. To prevent this forthcoming disaster many scientific studies are being conducted one of which is derivation of biodiesel from organic sources. Oleaginous substances can be converted to biodiesel using existing methods like catalyzed and non-catalyzed transesterification or microbial conversion processes. This paper is overview on catalyzed transesterification of waste cooking oil (WCO). Effect of high free fatty acid (FFA) and water content of WCO on the yield of biodiesel produced using acid and alkali catalytic reactions is discussed in the paper and the same is compared for pure oil. Further in the paper advanced processes of trans esterification, such as two step catalyzed transesterification and heterogeneous catalyzed processes are briefed. It is found that heterogeneous catalyzed process is more efficient as compared to homogenous catalyzed process hence it makes WCO cost effective raw material for the biodiesel production.*

1. INTRODUCTION

Biodiesel is an alternative diesel fuel which consists of alkyl esters and is derived from renewable sources like vegetable oils and animal fats [1-5]. Biodiesel is gaining popularity as an alternative fuel because conventional fossil fuels are on verge of depletion as well as due to its non-polluting and biodegradable nature [6, 7]. As all the organic carbon present in biodiesel is of photosynthetic origin it does not contribute in net rise in level of carbon dioxide and hence preventing greenhouse effect. It is an environmental friendly fuel and can be used without any modification in the present combustion engines. Figure 1 forecasts the increasing use of alternative fuels including natural gas, hydrogen and biofuels. Approximately 96% of all biodiesel produced annually is consumed presently. Also, the rate of production as well as consumption of biodiesel will go on increasing in the future as can be inferred from statistics in figure2. Region wise production rate is displayed in figure 3. After analyzing these statistics, it is evident that the technology for biodiesel production is being enhanced and will become more reliable and cost effective in the coming years. Biodiesel can be produced using any of the three chemical pathways Vis-a-Vis acid catalysis, alkali catalysis (collectively termed as chemically catalysis) and enzyme catalysis. Chemical catalyzed processes are preferred over enzyme catalyzed due to less reaction time and industrial ease of application [8]. Chemically, this reaction of producing Bio-diesel is called Trans esterification. Yields of biodiesel depend on reaction conditions and quality of oils. Biodiesel is produced from both edible as well as non edible oils like soybean, palm, sunflower, cotton seed, rapeseed, peanut oil, linseed oil, castor oil, jatropa and tungoil [7, 9].

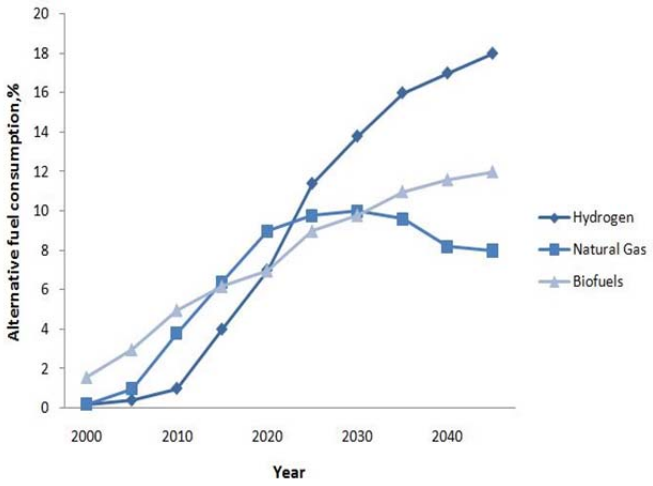

Fig. 1: Forecast for global consumption of alternative fuel [5]

2. TRANSESTERIFICATION

Transesterification is defined as conversion of oil into its corresponding fatty ester [12]. It is also defined as alcoholysis, the reversible reaction of a fat or oil with an alcohol to form esters and glycerol [1, 13].

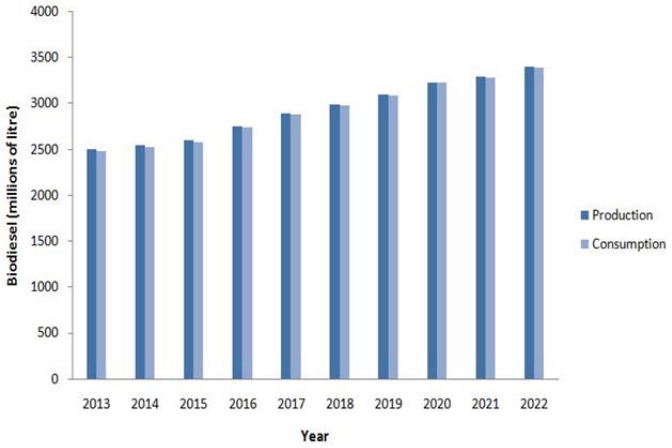

Fig. 2: Actual and prospective data on production and consumption of biodiesel [10]

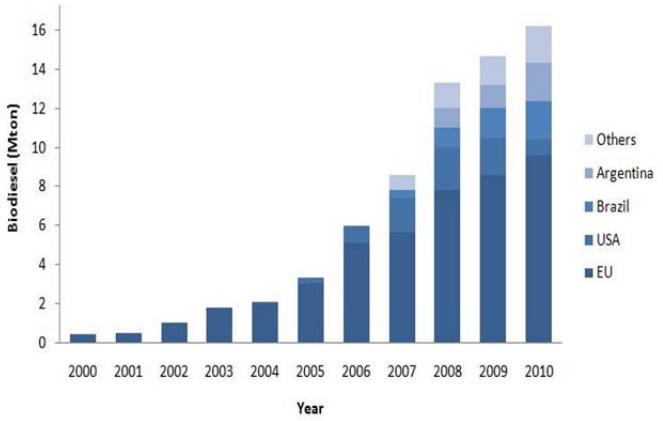

Fig. 3: Global biodiesel production from 2000 to 2010 [11]

Vegetable oils and animal fats are chemically, triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule [14]. Transesterification of triglycerides produce fatty acid alkyl esters and glycerol as final products [2]. Many factors such as oil quality, molar ratio of methanol to oil, type and amount of catalyst, time and temperature of the reaction affects the yield of esters. Fig 4 depicts the general reaction of the process. Where R1, R2, R3 are long hydrocarbon chains known as fatty acid chains. Transesterification reaction is reversible reaction hence addition of more alcohol shifts the reaction forward resulting in increase of biodiesel [13]. Some of the well known catalysts for alkali catalyzed transesterification includes NaOH, KOH, and $NaOCH_3$ and for acid catalyzed transesterification includes H_2SO_4, HCl, BF_3, H_3PO_4, etc. [13, 15]. Alkali catalyzed reaction are commercially more profitable as reaction rate is about 4000 time that of acid catalyzed [6].

The table 1 shows the work carried out for bio-diesel production from various feed stocks under different conditions using homogenous acid and base catalyst.

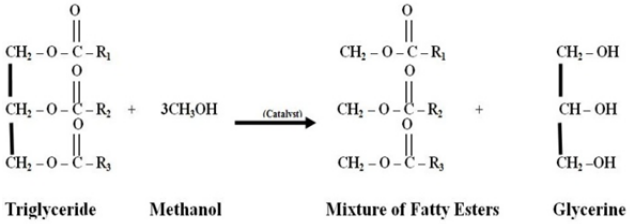

Fig. 4: General reaction for transestification [3,9]

3. EFFECT OF MOLAR RATIO

From stochiometry of the general reaction mentioned above in fig.4, it can be determined that three moles of alcohol reacts with one mole of triglyceride to yield 3:1 moles of fatty alkyl esters to glycerol [2]. But optimum ratio of alcohol to oil used for industrial purpose is 6:1, as excess alcohol shifts reaction forward to get yield as high as 98% [6]. There were many studies carried out to determine optimum molar ratio of alcohol to oil. Freedman *et al*. analyzed that soybean, sunflower, peanut, cotton behave similarly at molar ratio of 6:1 to achieve higher yield up to 98% [23]. Meher *et al.* has carried the study on transesterification of cynara oil where yield was measure for molar ratio range of 3:1 to 15:1; results showed that yield was higher in range of 9:1 to 12:1, for molar ratio 6:1 reaction was incomplete as presence of glycerin shifts reaction backward while for higher molar ratio of 15: 1 separation of glycerin became difficult [2]. Molar ratio of methanol to oil depends on type of catalyst and quality of raw oil. Freedman *et al*. performed the experiments on transesterification of soybean oil, and foundthat acid catalyzed transesterification required about 30:1 BuOH to oil ratio and alkali catalyzed reaction required a ratio of 6:1 to get same yield of ester [26]. Table 2 above gives clear picture about type and amount of catalyst required by pure oil and waste oil. Waste cooking oil consumes very high amount of catalyst to obtain yield upto 99%, at optimum temperature of 80^0C in 3h; whereas at same temperature and time pure oil requires molar ratio of 6:1 to achieve higher yields. Reasons for high consumption and type of catalyst are described in later sections.

4. EFFECT OF FFA AND WATER CONTENT

For transesterification process of crude vegetable oils, homogeneous catalysts including both acids and bases work efficiently but these catalysts are sensitive to FFA and water which is present in waste cooking oils. It is noted that presence of 5% FFA and 0.5% water by wt. reduces the yield of ester to less than 90% [27]. Potassium hydroxide (KOH), and sodium hydroxide (NaOH), act as effective catalysts for the transesterification of the waste cooking oil if the FFA content is <1% [26]**.** It is observed that if the FFA content is >1% and if an alkaline catalyst is used, amount of catalyst required to neutralize FFA is more [27, 28]. This additional

catalyst, required to neutralize the FFAs of the waste cooking oil, will affect the cost of the biodiesel. The excess addition of catalyst also gives rise to emulsion and increases the viscosity which leads to formation of gels [29]. Removal of this catalyst from the ester phase is not cost-effective.

Table 1: Homogeneous acid and base-catalyzed transesterification

Oil	Catalyst	Catalyst amount (%)	Alcohol wt.% oil	(O:M)	Reaction Conditions	Ester yield (%)	Ester conversion (%)	Reference
Waste Oils								
wco	H_2SO_4	4	Methanol	1:20	90^0C, 10h	-	>90	16
wco	NaOH	-	Methanol	-	25^0C, 1h	78%		17
wco	NaOH	-	Methanol	-	25^0C, 1h	86%		17
Pure Oils								
Refined soybean oil	NaOH	-	Methanol	-	25^0C, 1h	91% 1s		17
Karanja Oil	KOH	1	Methanol	1:6	65^0C, 2h 360rpm	98		18
Pongamia-pinnata	KOH	1	Methanol	1:10	60^0C, 1.5h		92	19
Rapeseed Oil	KOH	1	Methanol	1:6	65^0C,2h 600rpm	96		20
Sunflower Oil	NaOH	1	Methanol	1:6	60^0C,2h 600 rpm	97.1		21
Soybean Oil	H_2SO_4	0.5	Methanol	1:9	100^0C,8h 3.5 bar		99	22

Table 2: Yield of biodiesel in pure oil and waste cooking oil varying with molar ratio

Sr. No.	Oil	Molar ratio	Reaction conditions	Yield	Reference
1.	Waste cooking oil	Methanol	80^0C, 3h		24
		50:1	2.5% H_2SO_4	98%	
		100:1	3.5% H_2SO_4	98%	
		250:1	1.5% H_2SO_4	99%	
2.	Sunflower oil	Ethanol	80^0C, 3h 1%NaOH		25
		6:1		85%	
		8:1		80%	
		10:1		76%	
		12:1		70%	
		14:1		68%	

FFA has tendency to react with basic catalysts to form soap (fig.5) which leads to reduction in efficiency of catalyst and complicates the separation of glycerin from ester, ultimately reducing the yield hence alkaline catalyzed reactions are less preferred [1, 30]. Ester yield is affected by water as it supports saponification reaction and reaction of FFA with alcohol produces water which inhibits the reaction in case of acid-catalyst. Presence of water affects the yield in acid catalyzed reaction although it is relatively insensitive to FFA content. Water in waste oils hydrolyses oils and fatty acid methyl esters (FAME) in presence of strong acid or base catalysts. For transesterification, FFA and water content in oil must be less than 0.5(w %) and 0.06(w %) respectively [31, 32]. Acid-catalyzed esters have higher yields, compared to the base-catalyzed reaction, except for methyl esters. The only drawback for acid catalyzed reaction is that reaction time is very high [27]. Table 3 depicts about yields of ethyl as well as methyl esters from pure and waste oils under acid catalyzed and alkali catalyzed reactions. For pure oils alkali as well as acid catalyzed transesterification reactions give same yields, but alkali catalyzed reaction would be preferred over acid catalyzed because of high reaction rate. In case of waste cooking oils, yields are high and same for lower water content but in case of higher water content, yield for alkali catalyzed reaction has decreased, while in case of acid catalyzed yield of methyl ester is very low up to 6.2%. Reason for decline in yield of methyl esters in acid catalyzed reaction is polarity of methanol. It is a polar solvent hence form hydrogen bonds between oxygen of hydroxide and hydrogen of hydroxide, forming methanol clusters [27]. Presence of water, which is itself a polar solvent adds to the effect and hence further prevents action of catalyst and leads to reduction of methyl ester yield. Table 4 shows the comparative study of Berchmans *et al* on yield of biodiesel from Crude Palm Oil

(CPO), Net Coconut Oil (NCO) and crude Jatropha curcas seed oil (CJCO). All of these oils have high FFA content, the effect of which can be seen on the molar ratio, high amount of alcohol is consumed to achieve better yields in case of one step alkali catalyzed process [28]

Table 3: Yield of biodiesel in pure oil and waste cooking oil having water content [31]

Vegetable oil		Water content (wt. %)	Yield of methyl esters (wt. %)	
Pure Oils			**Alkali Catalyzed**	**Acid Catalyzed**
	Palm Oil	**2.1**	**94.4**	**97.8**
	Capparis Deciduas Oil	**2.0**	**65**	**-**
	Sesbania Sesban Oil	**2.0**	**29**	**-**
	Soybean Oil	**2.8**	**95**	
Waste Oils				
	Waste Cooking oil	**5.0**	**79.5**	**6.2 Methyl ester**
	Used Frying Oil	**0.2**	**94.4**	**97.8**
	Waste frying oil	**<0.3**	**98**	**-**
	Waste Cooking oil	**5.30**	**78.5**	**-**

Table 4: Yield of biodiesel in pure oil and waste cooking oil having FFA content [28]

Sr. No.	Oil	FFA%	Catalyst	Yield	Reaction Conditions	Reaction Type
1	CPO	7.2%	1% NaOH	80%	28:1 molar ratio	One step alkali catalyzed
2	NCO	1.8%	1% NaOH	85%	28:1 molar ratio	
3	CJCO	14.9%	3.3% NaOH	55%	70:1 molar ratio	
4	CJCO	14.9%	1% H_2SO_4 1% NaOH	90%	24:1	Twostep catalyzed process

Table 5: Yield of Biodiesel from Waste Cooking Oil (WCO) with high FFA content, using heterogeneous catalysts varying with oil to methanol molar ratio

Oil	FFA	Catalyst	Catalyst (wt. %)	(O:M)	Reaction condition	Yield (%)	Reference
WCO	1.04	Amberlyst 15	3	1:6 1:9 1:12 1:15	338K, 9h	62±1.21 66± 1.21 78 ±3.39 77 ±2.22	35
WCO	-	copper doped zinc oxide (CZO)	12	1:3 1:4 1:5 1:6 1:7 1:8 1:9	55^0C, 1h	36.12 57.36 87.11 93.48 95.61 97.73 93.48	36
WFO		CaO	10 3 2.5 8	1:12 1:9 1:8 1:9	60^0C,2 3 2.5 1	>95 96 95 97.2	37
WCO	1.176	KBr impregnated CaO	2 4 2	1:9 1:12 1:15	65^0C, 2h	62.3 78.9 61.58	38
WCO	17.5	Ferric- manganese doped tungstated/ molybdena	6	1:5 1:10 1:15 1:20 1:25	200^0C, 8h	68 76 83 90 95	39

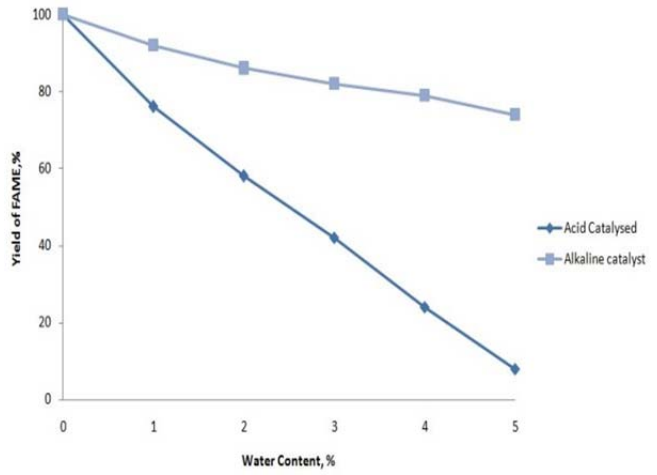

Fig. 6: Variation of ester yield with water content [31, 32, 33]

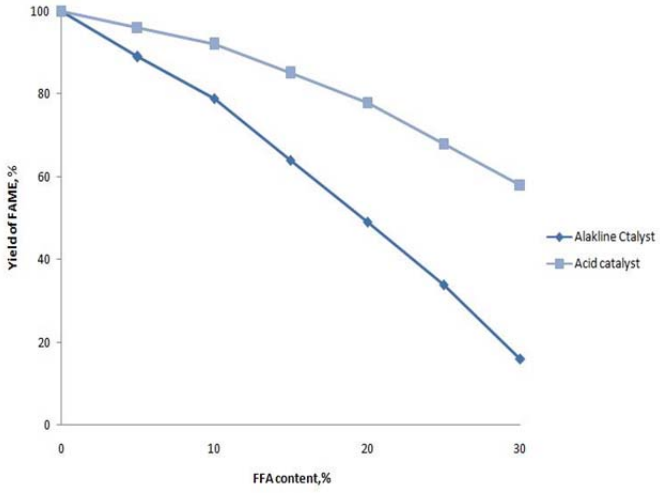

Fig. 7: Variation of ester yield with FFA content [33]

5. ADVANCED METHODS FOR TRANSESTERIFICATION

5.1 Two step catalyzed transesterification

As mentioned in the earlier section alkali catalyzed reaction, although it is more efficient in terms of time, gives very less yield in case of high water and FFA content, similarly acid catalyzed process has its own merits and demerits. To obtain higher yields from waste cooking oils, acid value of these oils must be < 2 mg KOH/g and FFA content must be less than 1% [34]. Pre-treatment of such oils is necessary, hence the two step catalyzed process was developed to improve the yield of biodiesel [4]. This process involves two major steps, esterification followed by alkali transesterification. Esterification reaction includes acid catalyzed conversion of free fatty acids into triglycerides which are then converted into Fatty esters by alkali catalyzed process. Reaction for two steps Acid- and Alkali- catalyzed can be summarized as shown in fig. 8. Table 5 shows the yields of biodiesel produced by using different types of heterogeneous catalysts in different reaction conditions as well as molar ratios of oil to methanol. As can be seen from the table minimum yield of ester obtained was 62% and went high up to 96%. Catalysts used for the reaction include ion exchange resins Amberlyst 15, solid base as well as solid acid.

6. CONCLUSION

Although pure oils showed better yields for alkali catalyzed transesterification, availability of pure oil can be a problem and can add to the cost of production hence this study reviewed and discussed the potential of waste cooking oil for production of biodiesel. In case of waste oils containing high FFA and water substantial decrease was found in the yield of biodiesel, when homogeneous alkali catalysts were used in comparison to pure oils.

Whereas acid catalyst reactions had very slow rate of reaction using either of the raw material but the amount of alcohol consumed was high in case of WCO. Therefore cost of biodiesel production from waste cooking oil increases using either alkali or acid catalyzed reactions. Heterogeneous catalytic process and two steps catalyzed process could overcome the disadvantages of using WCO as a raw material. Two steps catalyzed method combined the advantages of alkali and acid catalyzed processes and positive effect was obtained for the yields. Further the use of heterogeneous catalysts for transesterification gave better yields for biodiesel as compared to homogeneous catalysts. It also converted the complex two steps method into a single more efficient conversion process. Waste cooking oils can be cost effective instead of pure oils when heterogeneous catalytic transesterification process is used for production of biodiesel.

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