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RECENT DEVELOPMENT OF BIODIESEL FEED STOCK: A REVIEW

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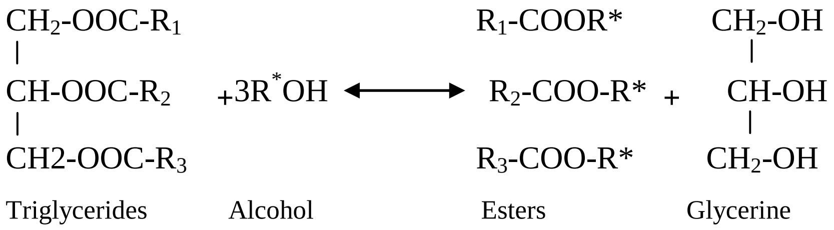
ABSTRACT

The depletion of fossil resources and environmental pollution are among the most critical problems that threat humanity. The attention is currently turned towards the use of biomass or biomass-derived materials as replacements to petroleum fuel. Direct use and blending of raw oils are among the early approaches where vegetable oils are used directly or diluted with petroleum diesel to run the engine. Thermal cracking that is the conversion of triglycerides to bio fuel with or without the presence of catalyst is another approach and it involves the use of high temperature in the absence of air or oxygen. As the process in an energy-intensive one, limited success has been achieved in such approach Recently, transesterification has been actively investigated as the most popular way to convert vegetable oils or animal fats into fatty acid methyl esters (FAME). Biodiesel is a clean burning diesel fuel with a chemical structure of fatty acid alkyl esters. Of the various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method.

Key Words - Biodiesel, Catalyst, Glycerides, Transesterification, Vegetable Oil

I. INTRODUCTION

The depletion of fossil resources and environmental pollution are among the most critical problems that threat humanity. The attention is currently turned towards the use of biomass or biomass-derived materials as replacements to petroleum fuel. In 1893, Rudolf Diesel attempted to make use of peanut oil as fuel for diesel engine. During 1930s and 1940s, vegetable oils replaced diesel fuels in many events, usually in emergency cases. In August 1982, the first international conference was held to discuss the use of vegetable oils as fuels. Many topics were highlighted including the cost of fuel, plausible methods of manufacturing, the characterizations of the fuel and the effects of fuel derived from vegetable oil on the efficiency of diesel engines. It is an eco friendly fuel and biodegradable. Besides being non toxic, it is mainly free of sulphur components and aromatics. Biodiesel can mix at any percentage with petroleum fuel or it can itself be used as a successful fuel. There are four different methods to produce biodiesel from bio resources. Thermal cracking that is the conversion of triglycerides to bio fuel with or without the presence of catalyst is another approach and it involves the use of high temperature in the absence of air or oxygen. As the process in an energy-intensive one, limited success has been achieved in such approach. Recently, transesterification has been actively investigated as the most popular way to convert vegetable oils or animal fats into fatty acid methyl esters (FAME). Fig.1.1 illustrates the general equation of transesterification reaction. It is the organic reaction that causes the exchange of organic group (R'') of an ester with the organic group (R') of an alcohol where, R1, R2, R3 are long-chain hydrocarbons, usually called fatty acid chains. The main types of fatty acids in vegetable oils and animal fats are such as palmitic, myristic, stearic, oleic, linoleic and linolenic.



$$\begin{array}{l} CH_2\text{-}OOC\text{-}R_1 \\ | \\ CH\text{-}OOC\text{-}R_2 \\ | \\ CH2\text{-}OOC\text{-}R_3 \end{array} + 3R^{*}OH \longleftrightarrow \begin{array}{l} R_1\text{-}COOR^{*} \\ \\ R_2\text{-}COO\text{-}R^{*} \\ \\ R_3\text{-}COO\text{-}R^{*} \end{array} + \begin{array}{c} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

Fig1.1 General-Glyceride transesterification to biodiesel

Transesterification mechanism consists of a series of consecutive reversible reactions. Triglyceride molecules react step by step with methanol to form diglyceride, monoglyceride and in the last step, glycerol is formed Fig.1. 2 One mole of FAME is generated in each step of the transesterification process. All of these reactions are reversible and essentially the goal in this reaction is to shift the equilibrium to the products side, forming more fatty acid esters and glycerol. Usually, methanol is used in the biodiesel production process as it is relatively cheap compared to other alcohols and has small chain of carbon. However, as of the reaction is reversible, excess alcohol is needed to shift the reaction to form more products. This reaction is commonly catalyzed by acid or base catalysts while another possibility could be through the use of enzymatic catalyst (biocatalysts) especially lipases. Biodiesel production process has undergone significant progress in recent years with some innovations introduced to improve efficiency and productivity.

$$TG+CH_3OH \longleftrightarrow DG+FAME$$

$$DG+CG3OH \longleftrightarrow MG+FAME$$

$$MG+CH3OH \longleftrightarrow GLY+FAME$$

Fig.1.2 The sequence of transesterification reaction

II. CLASSIFICATION OF TRANSESTERIFICATION

There are two types of transesterification

2.1 Catalytic process

2.1.1 Homogeneous catalyst

2.1.2Non-homogeneous catalyst

2.1.3Enzyme-Catalyzed Transesterification

2.2 Non-catalytic process

2.2.1 Supercritical method by using ethanol or methanol.

III. CATALYTIC PROCESS

3.1 Acid transesterification

The acid value is a measure of the number of acidic functional groups in a sample and is measured in terms of the quantity of potassium hydroxide required to neutralize the sample. Acid value of the feed stock for alkaline transesterification has to be reduced to less than 2.0 mg KOH/g. However, other authors advocate it to be less than 4.0 mg KOH/g. The commonly used catalyst during acid esterification of neat oil is sulphuric acid. Nevertheless, this process too has a drawback as water is produced along with ester from the reaction of FFA with alcohol which inhibits the transesterification of glycerides. For waste cooking oil to the acid employed is sulphuric acid . But in this case, the conversion reported is low (82%) and the alcohol required for the reaction is high. (Wang *et al*,2007) tried a new catalyst Fe2(SO4)3 (ferric sulphate) as an alternate to sulphuric acid and have reported much better conversion (97.02%). As, ferric sulphate is insoluble in oil, it was centrifuged from the liquid after acid esterification and reused for the next batch. High temperature and high concentration of H_2SO_4 as catalyst could burn some of the oil which will then cause low yield of biodiesel product.

3.2 Alkaline transesterification

For oil samples with FFA below 2.0%, alkaline transesterification is preferred over the acid catalyzed transesterification as the former is reported to proceed about 4000 times faster than the latter. The common catalyst employed during alkaline transesterification at industrial level application includes the homogeneous catalysts sodium hydroxide, potassium hydroxide, etc. The use of homogeneous catalyst such as sodium hydroxide and potassium hydroxide has been successful at industrial level for production of biodiesel. However, the biodiesel and glycerin produced have to be purified to remove the basic catalyst and need its separation by washing with hot distilled water twice or thrice. Thus, heterogeneous catalyst has also been tried by researchers to overcome this drawback of time consumption and colossal consumption of water. The heterogeneous catalyst can be separated from the final product by filtration which checks time consumption and prevents the consumption of large volume of water. The filtered solid then can be reused.

3.3 Enzyme-Catalyzed Transesterification

Recently, it has been found that enzymatic catalyst (immobilized lipase) can be used in transesterification reaction. No by product, easy product removal, reusability without any separation step and lower operating temperature are the key advantages of this method. However, it is found to be very expensive .The enzymatic reaction is insensitive to water and FFA content in waste cooking oil. (Ranganathan *et al*, 2008) compared the alkali and enzymatic transesterification process in biodiesel production. They construed that the utilization of biocatalyst can produce very high purity FAME with lower or no downstream process compared to alkali catalysts.

IV. NON-CATALYTIC PROCESS

4.1 Supercritical method

One of the approaches to overcome problems associated with poor immiscibility between the reactants and technical problems caused by catalysts is to use supercritical method. In this approach , no catalyst is involved. Supercritical alcohol transesterification reaction takes place under extremely high temperature and pressure. When a gas or liquid is exposed to pressure and temperature beyond its critical point, unusual phenomena on its properties are exhibited. Liquid and vapour phase are no longer confined under these conditions and single supercritical fluid phase is generated. In the supercritical method, methanol and oil, which are immiscible liquids at room temperature, will form a homogenous fluid.

V. TYPE OF CATALYST USED IN PRODUCTION OF BIODIESEL

5.1 Homogeneous catalyst

Generaly used homogeneous catalyst are Sulfuric acid, KOH, NaOH.

5.2 Hetrogeneous catalyst

Hetrogeneous catalysts are used CaO, CaO/Li, CaO/KF, MgO, MgO/Li, SrO, ZnO, ZnO/Li, ZnO/Li, ZnO/Ba,ZnO/KF, ZrO_2, ZrO_2/SO_4^{2-}

Advantages and disadvanatages at different type of catalysts used in the biodiesel production.

Type	Example	Advantages	Disadvantages
Alkali Homogeneous	NaOH, KOH	High catalytic activity, low cost, favourable kinetics, modest operation conditions	Low FFA requirement, anhydrous saponification, emulsion formation wast water from purification
Heterogeneous	Cao,$CaTiO_3$,$CaZrO_3$, CaO,CaO_3,$CaMnO_3$, $Ca_2Fe_2O_3$,KOH/Al_2O_3	Noncorrosive, environmentally benign ,recyclable, fewer disposal	Low FFA Requirement , more wastewater from purification, molar ratio of alcohol to oil require high reaction temp
Acid Homogeneous	Concentrated sulphuric acid	Catalyze esterification and transesterification simultaneously avoid soap formation	Equipment corrosion, diffucult to recycle, reaction temperature
Hetrogeneous	ZnO/I_2,ZrO_2/SO_4^{2-} TiO_2/SO_4^{2-},Carbon-based solid acid catalyst	Catalyze esteriofication and transesterification simultaneously,recyclable, ecofriendly	Low acid site concentrations,low microporosity, diffusion limitation cost

VI. VEGETABLE OIL COMPOSITION

Natural oils and fats are the esters of glycerol and fatty acids. They are called glycerides or triglycerides. There are two kinds of fatty acids: saturated fatty acids are polarized and contain a single carbon bond, while unsaturated fatty acids include one or more carbon-to-carbon doubled bonds and are polarized. Examples of common fatty acids are stearic, oleic, linolenic and palmitic. table 6.1 and table 6.2 show the % composition of fatty acid.

Table 6.1-vegetable oil composition (Goering *et al*,1982)

vegetable oil	**Fatty acid composition (% weight)**								
	16:1	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	11.67	1.85	0.24	0.00	0.00	25.16	0.00	60.60	0.48
Cottonseed	28.33	0.89	0.00	0.00	0.00	13.27	0.00	57.51	0.00
Crambe	20.7	0.70	2.09	0.80	1.12	18.86	58.51	9.00	6.85
Peanut	11.38	2.39	1.32	2.52	1.23	48.28	0.00	31.95	0.93
Rapeseed	3.49	0.85	0.00	0.00	0.00	64.4	0.00	22.30	8.23
Soyabean	11.75	3.15	0.00	0.00	0.00	23.26	0.00	55.53	6.31
Sunflower	6.08	3.26	0.00	0.00	0.00	16.93	0.00	73.73	0.00

Table 6.2 -typical fatty acid composition-common oil source

Fatty acid	soyabean	cottonseed	palm	Lard	tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0.0

VII. VARIOUS RAW MATERIALS USED AS FEED STOCK

7.1 Conventional feed stock

Mahua Soybean , Nile tilapia Rapeseed ,Palm Canola,Poultry Babassu , Tobacco seed ,Brassica, carinata , Rubber plant, Brassica napus, Rice bran Copra , Sesame ,Groundnut , Sunflower Cynara, cardunculus, Barley Cottonseed , Coconut Pumpkin , Corn Jojoba oil , Used cooking oil,Linseed Peanut ,Mustard Olive oil.

7.2 Non-conventional stock

Lard, Tallow,Poultry fat,Fish oil,Brassica carinata Bacteria, Algae ,Fungi,Micro-algae,Tarpenes, Latexes,Pongamina pinnata, Palanga,*Jatropha curcas*,Sea mango,Okra. (Leung and Guo,2006) compared the transesterification reaction conditions of neat canola oil with used frying oil (UFO). A comparatively higher temperature (333 K), higher molar ratio (7:1, methanol/UFO), and more amount of catalyst (1.1 wt% NaOH) was needed when compared to edible canola oil where optimal conditions were 315–318 K, 6:1 methanol/oil molar ratio and 1.0 wt% NaOH. However, comparatively a less time (20 min) was needed in UFO for completion of reaction in comparison to canola oil where reaction time took 60 min. Non-edible oils used for transesterification mostly are the oils with higher free fatty acids such as rubber (*Ficus elastica*), jatropha (*J. curcas*), karanja (*Pongamia pinnata*), mahua (*Madhuca indica*), polanga (*Calophyllum inophyllum*), tobacco (*Nicotina tabacum*), etc. (Miao and Wu,2006)reported production of biodiesel from microalga C. protothecoides using 100% catalyst quantity (based on oil weight) with 56:1 molar ratio of methanol to oil at temperature of 303 K in 4 h of reaction time.

Table 7.1 Biodiesel production from different feedstock

Feed stock	Transesterific-ation	alcohol	Molar ratio (methanol	catalyst	Reaction temperature	Yield
Sunflower	Single stage	Supercritical methanol	40:1	No catalyst	473-673	78-96%
Pongamiya pinnata	Single stage	methanol	10:1	KOH (1% by wt)	378	27%
Madhuca indica	Two step	Methanol	0.3-0.35 v/v	1% v/v H_2SO_4	333	98%
Rubber seed	Two step	methanol	6:1	H_2SO_4 0.5% by	318±5	98%
Chlorella Prothecoides		methanol	56:1	Acid catalyst	303	>80%

Chlorella protothecoides		methanol	56:1	H_2SO_4 (100%)	303	63%
Neat canola	single	methanol	6:1	NaOH 1.0 WT%	318	98%
Nicotiana Tabacum L	Two step	methanol	18:1	H_2SO_4 (1% with	333±0.1	91%
Pongamia pinnata	Single step	methanol	6:1 12:1	KoH (1% wt)	338	97-98%
Soyabean		methanol	4.5:1	TiO_2/ZrO_2 (11wt%Ti)	448	95%
Soyabean	Single step alkali	methanol	6:1	NaOH	318	100%
Jatropha,pongamia,sunflower	Single step	methanol	3:1	NaOH/KOH (1%by wt)	-	-
Calophyllum innophylum	Three step zero catalysed	methanol	6:1	anhydrous H_2SO_4	338	85% yield in 90 min
Jatropha curcas	Two step acid catalysed	methanol	0.28 v/v	H_2SO_4 1.43%v/v	333	>99%
Triolein	Single step	ethanol	10:1	Anion exchange	323	98.8%
Sunflower oil	Single step	methanol	13:1	Activated CaO(1% wt)	333	-
Karanja oil	Two step	methanol	8:1	H_2SO_4	318±2	89.5%

Source :(Y.C. Sharma et al. Fuel 87(2008) 2355-2373)

VIII. EFFECT OF DIFFERENT PARAMETERS ON PRODUCTION OF BIODIESEL

8.1 The effects of moisture and free fatty acids

The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult. Bradshaw and Meuly (1944) and(Feuge and Grose ,1949)also stressed the importance of oils being dry and free (<0.5%) of free fatty acids.(Freedman et al,1984) stated that ester yields were significantly reduced if the reactants did not meet these requirements.

8.2 The effect of molar ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while a alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman et al.,1986). Bradshaw and Meuly (1944) stated that the practical range of molar ratio was from 3.3 to 5.25:1 methanol to vegetable oil. The ratio of 4.8:1 was used in some examples, with a yield of 97±98%, depending upon the quality of the oils.

8.3 Effect of catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed. However if a glycerine has a higher free fatty acid content and more water, acid-catalyzed transesterifcation is suitable . The acids could be sulphuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, potassium amide and potassium hydride. Sodium methoxide was more effective than sodium hydroxide because of the assumption that a small amount of water was produced upon mixing NaOH and MgOH. The opposite result was observed by (Ma et *al*, 1998). NaOH and NaOCH3 reached their maximum activities at 0.3 and 0.5% w/w of beef tallow, respectively.

8.4 The effect of reaction temperature

Transesterification can occur at different temperatures, depending on the oil used. In methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20±35°C with a molar ratio of 6:1± 12:1 and 0.005±0.35% (by weight of oil) of NaOH catalyst (Smith, 1949). For the transesterification of refined soybean oil with methanol (6:1) using 1% NaOH, three different temperatures were used (Freedman *et al*, 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of ester.

IX. QUALITY CONTROL

For commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets international standards specifications have been set but the ASTM D 6751 and EN 14214 standards are the most commonly used standards. Even in blends with conventional diesel fuel, (Mit- telbach,1996) stated that most people in the industry expect the biodiesel blending stock to meet the relevant standard before being blended. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with distillate fuels.

X. CONCLUSION

Biodiesel is a clean burning diesel fuel with a chemical structure of fatty acid alkyl esters.The alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method. Transesterification is basically a sequential reaction. However, when the raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps and the water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. These are undesirable reactions which reduce the yield of the biodiesel product. Therefore, after refining the raw materials, the acidic feedstock's should be pre-treated to inhibit the saponification reaction. There are three primary approaches for reducing the amount of free fatty acids: esterification of free fatty acids with methanol, in the presence of acidic catalysts; using iodine as a catalyst; adding glycerol into the acidic feedstock with a catalyst like zinc chloride and heated to a high temperature. For refining the crude biodiesel produced, the product should first be neutralized and then put through an alcohol stripper before cleaning by either one of the following approaches: water washing, membrane extraction, and dry washing. As a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure that it meets international standards even if it has been stored for a long time.

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