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Comparison between Biodiesel Production from Raw Vegetable Oil and Waste Cooking Oils

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ABSTRACT: This project emphasis on the comparison between production of biodiesel from raw vegetable oil and its waste cooking oils. The objective is to determine which oil gives good efficiency for production of biodiesel. The feedstock for biodiesel production is usually vegetable oil, pure oil or waste cooking oil, or animal fats. The most common way today to produce biodiesel is by transesterification of the oils with an alcohol in the presence of an alkaline catalyst. It is a low temperature and low-pressure reaction. It yields high conversion (96%-98%) with minimal side reactions and short reaction time. It is a direct conversion to biodiesel with no intermediate compounds. This work provides an overview concerning biodiesel production. Likewise, this work focuses on the commercial production of biodiesel. Comparison of the optimum conditions of alkaline-catalyzed transesterification process for biodiesel production from pure sunflower, palm cooking oil and its waste cooking oil through transesterification process using alkaline catalysts was studied. To obtain a high quality biodiesel fuel that comply the specification of standard methods (ASTM). The highest approximately 99.5% biodiesel yield acquired under optimum conditions of 3:1 volumetric oil-to-ethanol ratio, 3.7g NaOH catalyst at 50°C reaction temperature. Result showed that the biodiesel production from Pure Oils had lesser efficiency than Waste Oils. The research demonstrated that biodiesel obtained under optimum conditions from Waste Cooking Oil was of good quality and could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying.

KEYWORDS: Biodiesel, Transesterification, Sunflower oil, Palm oil and Waste cooking oil

I. INTRODUCTION

AN OVERVIEW OF BIODIESEL:

Nowadays, majority of the worlds energy needs are supplied through petrochemicals sources. All these sources are finite and at current usage rates will be consumed shortly. The high energy demand in the industrialized world as well as the pollution problems caused due to the use of fossil fuels make it increasingly necessary to develop a new renewable energy source. Biodiesel is an attractive alternative to fossil fuels; it is biodegradable, non-toxic and has low emission profiles as compared to petroleum fuels. Biodiesel is carbon-neutral. The amount released CO₂ by burning biodiesel is the same amount CO₂ absorbed during the formation of the raw material.

Compared to petroleum-based diesel, the high cost of biodiesel is the major barrier to its commercialization. Its cost, which is approximately one and a half times that of petroleum-based diesel, depends on feedstock oils. It is reported that approximately 70-95% of the total biodiesel production cost arises from the cost of raw material, that is, vegetable oil or animal fats. Waste cooking oil (WCO) is a domestic waste generated as the result of cooking and frying food with edible vegetable oil. WCO has been identified as an alternative source of fatty materials for the production of biofuels. WCO and fats produce significant disposal problems in many parts of the world.

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WHY BIODIESAL?

It's Economical

Biodiesel can be produced by individuals on a small scale relatively inexpensively when compared to Petrodiesel. With prices that low, most people are able to save thousands on their fuel bills. With savings like that, most people are able to recoup the initial investment on the equipment needed to make biodiesel within a matter of months.

It's Renewable

Biodiesel has been touted far and wide for its renewable properties. Instead of making a fuel from a finite resource such as crude oil, Biodiesel can be produced from renewable resources such as organic oils, fats, and tallow's. This means that it can be made from things that can be regrown, reproduced, and reused. So, if you need more, you can just grow another crop of seeds for the oil.

It's Good For the Environment

When Biodiesel is used to power diesel engines, the emissions at the tailpipe are significantly reduced. Carbon Dioxide, Hydrocarbons, and ParticulateMatter (the black smoke from diesels) all are significantly reduced when Biodiesel is used. When used in older diesel engines such as indirect combustion diesels, the results are astounding. There was a reduction in the tailpipe emissions of nearly 90%. It also has a positive energy balance.

It supports farmers

When Biodiesel is made from organic oils such as Canola, Soy, Peanut, or otherdomestically grown seed crops, it helps the farming community out. Because the oil used to make Biodiesel is "domestically grown", it keeps the money flowing to those that "grow" the feedstock. This continues to help out the renewable aspect of Biodiesel because this means more seed crops can be grown by local farmers.

It reduces dependency on Crude Oil

When Biodiesel is used in place of petrodiesel, it reduces the amount of crude oil used up. This means that it helps to reduce our dependence on a limited resource and increases our use of renewable resources. We think that's a great step toward reducing our dependence on a fuel that may not be around forever.

It's good for the engine

Biodiesel, unlike Petrodiesel, has a much higher "lubricity" to it. This means that it's essentially "slipperier" than normal diesel fuel. With the added "lubricity" of Biodiesel, engines have been shown to experience less wear and tear when used on a regular basis. Also, because Biodiesel is less polluting, it means that it's easier on the engine.

It's the perfect alternative fuel

When compared to several other Alternative Fuels available, Biodiesel comes out way ahead. Most alternative fuels require changes to a vehicle to be used. Natural Gas & Propane require special tanks to be installed and changes to the fuel injection system must be made as well. Ethanol also requires specialized changes to the fuel injection system. Electricity requires a completely different engine. In most cases, once a vehicle undergoes the conversion necessary to run the alternative fuel, there's no going back. You either run the alternative fuel or you don't run the vehicle.

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II. BIODIESEL FEATURES

The biodiesel properties depend on the used feedstock (new vegetable oil, waste cooking oils, animal fats, etc).

Important properties of the biodiesel are:

- It can be used pure or blended with petrodiesel in engines
- It can be used in the diesel engine without any modifications.
- It can be stored in the same containers than petrodiesel
- It can prolong engine life due to the higher lubrication capacity
- It improves combustion process. The biodiesel contains at least 11% oxygen.

Moreover those advantages also other economic aspects can be taken into account:

- a) Biodiesel contribute to diversification of energy sources. It is an important aspect for countries without fossil fuel sources.
- b) The biodiesel contributes to agricultural and rural development.

The most important biodiesel disadvantages, comparison with the fossil fuel, are:

- a) Lower long-term storage stability. The biodiesel becomes rancid due to oxidation and bacterial air. This rancidity process produces aldehydes, ketones and acids, which have strong and unpleasant odors.
- b) The biodiesel needs more additives, mainly in cold countries, due to its high cloud point.

BIODIESEL PRODUCTION METHODS:

Biodiesel production is the process of producing the biofuel, biodiesel, through the chemical reaction transesterification and esterification. This involves vegetable or animal fats and oils being reacted with short-chain alcohols (typically methanol or ethanol).

1) *Supercritical process:*

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.

2) *Ultra- and high-shear in-line and batch reactors:*

Ultra- and High Shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This drastically reduces production time and increases production volume.

The reaction takes place in the high-energetic shear zone of the Ultra- and High Shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size the larger the surface area the faster the catalyst can react.

3) *Ultrasonic reactor method:*

In the ultrasonic reactor method, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This cavitation simultaneously provides the mixing and heating required to carry out the transesterification

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process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Hence the process of transesterification can run inline rather than using the time consuming batch processing. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

4) Lipase-catalyzed method:

Large amounts of research have focused recently on the use of enzymes as a catalyst for the transesterification. Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high free fatty-acid content, which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not in-activated and can be used for several batches, making the lipase system much more cost effective.

5) Volatile Fatty Acids from Anaerobic Digestion of Waste Streams:

Lipids have been drawing considerable attention as a substrate for biodiesel production owing to its sustainability, non-toxicity and energy efficient properties. However, due to cost reasons, attention must be focused on the non-edible sources of lipids, in particular oleaginous microorganisms. Such microbes have the ability to assimilate the carbon sources from a medium and convert the carbon into lipid storage materials. The lipids accumulated by these oleaginous cells can then be transesterified to form biodiesel.

REACTION

Transesterification is the process of separating the fatty acids from their glycerol backbone to form fatty acid esters (FAE) and free glycerol.



General Aspects of Transesterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Scheme 1). In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.



Scheme 1. General equation for a transesterification reaction.

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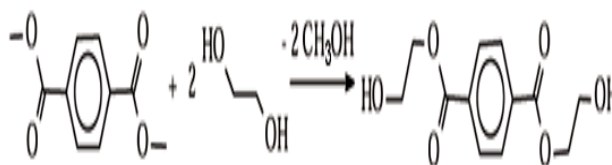
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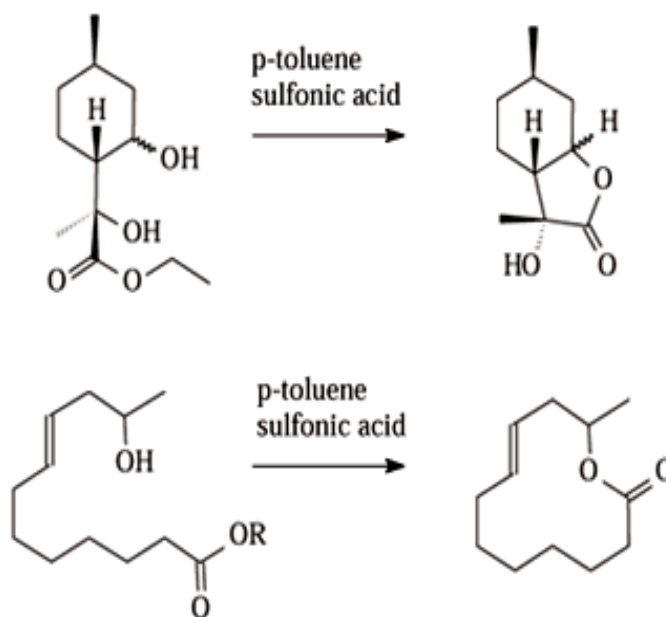
The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds. An example is the production of PET (polyethylene terephthalate), which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst (Scheme 2).

Furthermore, a large number of acrylic acid derivatives is produced by transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts



Scheme 2. Transesterification of dimethylterephthalate with ethylene glycol.

If the alcohol and the ester groups are present in the same molecule simple lactones or macrocycles are formed by an intramolecular transesterification, as shown in Scheme 3. Further transesterification reactions can be found in the literature, in which metal alkoxides, aluminum isopropoxide, tetraalkoxytitanium compounds and organotin alkoxides are applied as catalysts



Scheme 3. Examples of intramolecular transesterification reactions, forming lactones or macrocycles.

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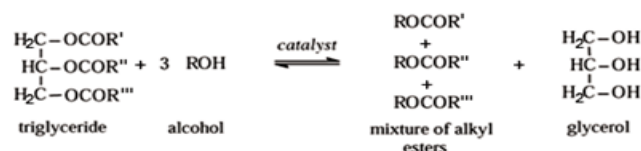
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Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol (Scheme 4). The overall process is a sequence of three consecutive and reversible reactions, in which di- and monoglycerides are formed as intermediates. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed.

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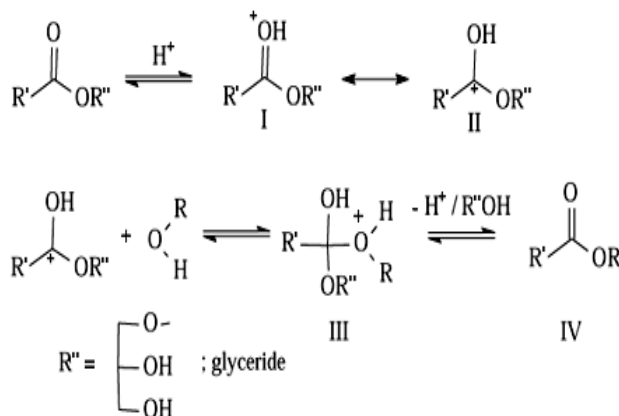


Scheme 4. Transesterification of vegetable oils.

Acid-Catalyzed Processes

The transesterification process is catalyzed by Brønsted acids, preferably by sulfonic²⁷ and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion³⁰. The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Scheme 5, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation I which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H⁺.



R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 5. Mechanism of the acid-catalyzed transesterification of vegetable oils.

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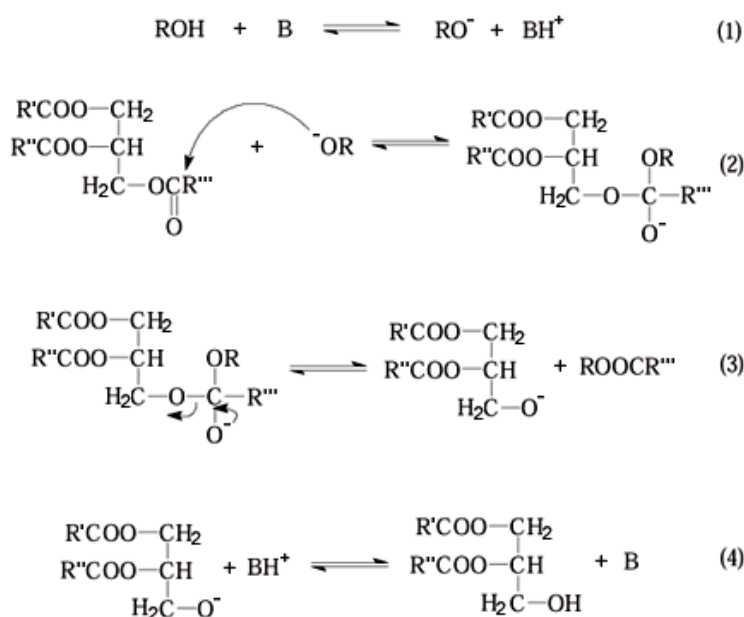
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According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates. The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme 6. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.



Scheme 6. Mechanism of the base-catalyzed transesterification of vegetable oils.

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes.

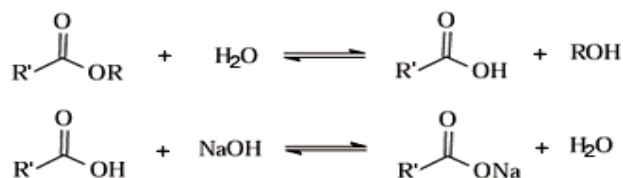
Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Scheme 7). This undesirable saponification reaction reduces the ester yields and considerably difficult the recovery of the glycerol due to the formation of emulsions.

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R' = carbon chain of the fatty acid

R = alkyl group of the alcohol

Scheme 7. Saponification reaction of the produced fatty acid alkyl esters.

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation. This can be explained by the formation of bicarbonate instead of water (Scheme 8), which does not hydrolyse the esters.



Scheme 8. Reaction of potassium carbonate with the alcohol.

Lipase-Catalyzed Processes

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools.

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.

Non-Ionic Base-Catalyzed Processes

In order to obtain milder reaction conditions and to simplify manipulations, a great number of organic bases has been developed and used as catalyst or reactant for organic syntheses.

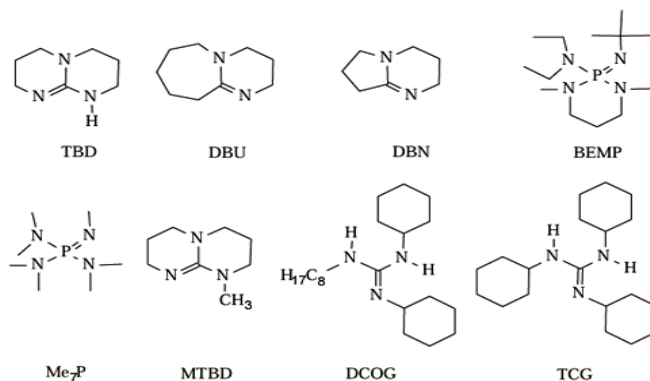
Among these bases, amines such as triethylamine, piperidine, 1,2,2,6,6-pentamethylpiperidine, pyridine, 2,6-di-*tert*-butylpyridine and 4-dimethyl-aminopyridine(DMAP); amidines such as 1,8-diazabicyclo[5.4.0]undec-7-en(DBU)and 1,5-diazabicyclo[4.3.0]non-5-ene(DBN); guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,1,3,3-tetramethylguanidine (TMG), 1,1,2,3,3-pentabutylguanidine (PBG), 1,3-diphenylguanidine, 1,2,3-triphenylguanidine and amino- and nitroguanidines; triamino(imino)phosphoranes such as *tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorane(BEMP) and tris(dimethylamino)methyliminophosphorane (Me₇P), shown in Scheme 9, are frequently used in organic synthesis.

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Scheme 9. Molecular structures of some non-ionic organic bases.

The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied. In a first series of studies, the catalytic activity of some guanidines was compared to that observed using other bases such as the amidines DBU and DBN, and the triamino(imino)phosphoranes BEMP and Me₇P

It was observed that TBD, even if applied at only 1 mol%, produces more than 90% of methyl esters after 1 h. Using the other bases, under the same experimental conditions, the yields were not higher than 66% (Table 1). The order of the catalytic activity is not directly related to the relative basicity of these compounds, since BEMP and Me₇P should be the more efficient catalysts, followed by TBD. However, the guanidines are more active catalysts and the activity follows their relative basicity.

Table 1. Comparison of the catalytic activity of some guanidines, amidines and triamino(imino)phosphoranes in the transesterification of rapeseed oil with methanol.

Catalyst	Relative basicity ⁵¹	pKa (CH ₃ CN) ⁴⁹	Yield (%) after 1 h ^a
TBD	150	25.9	91
BEMP	6873	not available	66
Me ₇ P	4762	27.52	63
MTBD	43.65	25.43	47
DBU	3.4	24.32	32
TMG	0.95	23.30	18
DBN	1	23.79	4.5

a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.

According to the observed results and to the mechanism of the base-catalyzed transesterification (Scheme 6), it seems that the good performance of TBD, when compared to BEMP and Me₇P, is related to its kinetic activity. The catalytic site (unshared electron pair of the sp²N) of TBD is practically unhindered (Scheme 10), allowing an easy access of the methanol for proton transfer, while the steric hindrance shown by the triamino(imino)phosphoranes is so significant that they are practically inert to alkylating agents, such as isopropyl bromide, as well as extremely resistant to react with thionyl chloride and thiophosgene.

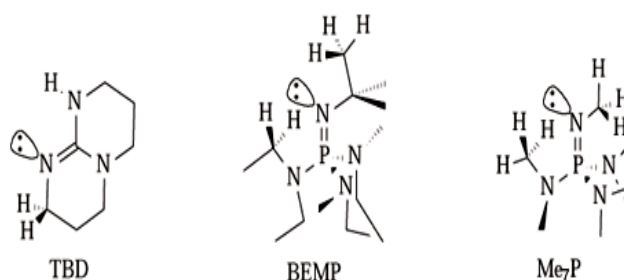
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Other bases such as DMAP, pyridine and triethylamine were also tested. However, even at 5 mol%, these amines did not give satisfactory yields. DMAP was the most active within this series, producing only 20% of methyl esters after 1 h.



Scheme 10. Steric hindrance of TBD, BEMP and Me₇P.

In a second series of studies, the catalytic activity of TBD was compared to that observed for typical industrial catalysts (*e.g.* NaOH and K₂CO₃). The results of this study are shown in Table 2.

The reaction yields obtained with TBD were close to those observed with NaOH and no undesirable by-products such as soaps (easily formed when alkaline metal hydroxides are used) were observed. When compared to potassium carbonate, TBD was always more active, even at low molar concentrations. Although TBD is less active than sodium methoxide (at only 0.5%, CH₃ONa produces more than 98% of methyl esters after 30 min), its use does not require any special condition.

Table 2. Comparison between TBD and the conventional inorganic catalysts.

Catalyst	Yield (%) after 1 h ^a
NaOH (1 mol%)	98.7
K ₂ CO ₃ (1 mol%)	84.0
K ₂ CO ₃ (2 mol%)	90.3
K ₂ CO ₃ (3 mol%)	92.4
TBD (1 mol%)	89.0
TBD (2 mol%)	91.4
TBD (3 mol%)	93.0

^a: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 h, 70 °C.

Due to the excellent performance of TBD in the transesterification of vegetable oils, the catalytic activity of other alkylguanidines was also investigated, in order to establish and understand all factors that may affect their catalytic properties. In a third series of studies, the catalytic activity of several alkylguanidines was compared.

TBD was always the most active, however, 1,3-dicyclohexyl-2-*n*-octylguanidine (DCOG), 1,1,2,3,3-pentamethylguanidine (PMG), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) and 1,2,3-tricyclohexylguanidine

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(TCG), also showed a good catalytic performance⁶⁴. The activity order of the catalysts TBD > TCG > DCOG > MTBD > PMG (Table 3) corresponds to their relative base strength, which is increased by structural factors such as number and type of substituents (cyclic or acyclic chain)⁵¹. The excellent performance of DCOG and TCG is also assigned to the high symmetry of their guanidinium cations, as observed earlier for the symmetric 1,2,3-trimethylguanidine.

Table 3. Transesterification of rapeseed oil with methanol using the most active alkylguanidines as catalysts.

Catalyst	Yields (%) after 1 h ^a		
	1 mol%	2 mol%	3 mol%
TBD	90	91	93
DCOG	74	80	92
TCG	64	91	92
MTBD	47	74	-
PMG	49	67	90

a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.

Results obtained in the transesterification of soybean oil with methanol show that 1,2,3,4,5-pentacyclohexylbiguanidine (PCBG) is even more active than TCG, as a 82% yield of methyl esters is obtained with PCBG after 1 h, compared to 69% with TCG under the same condition.

Heterogeneously Catalyzed Processes

The advantage of using guanidines in the transesterification of vegetable oils is the possibility to heterogenize them on organic polymers. The heterogenization of unsubstituted guanidines can be achieved by their reaction with microcrystalline cellulose activated by cyanuric chloride at the C-6 position (Scheme 11).

After deprotonation of the guanidinium salt formed, the guanidine-containing cellulose shows a slightly reduced activity, compared to guanidine in homogeneous phase, giving a conversion of 30% after 1 h, when used at 5 mol%.

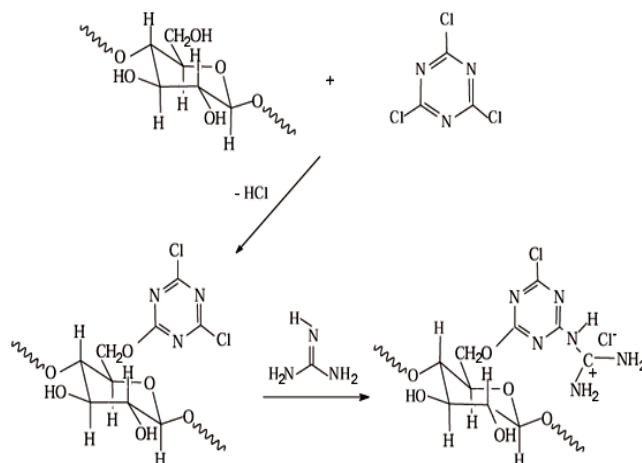
This guanidine-containing cellulose was used in a continuous reactor containing 100 g of the catalyst. An alcohol/oil mixture of 2:1 was pumped at 60 °C with a rate of 0.48 L/h. In the first hour the methyl esters were obtained with high yields and the phase separation was quick.

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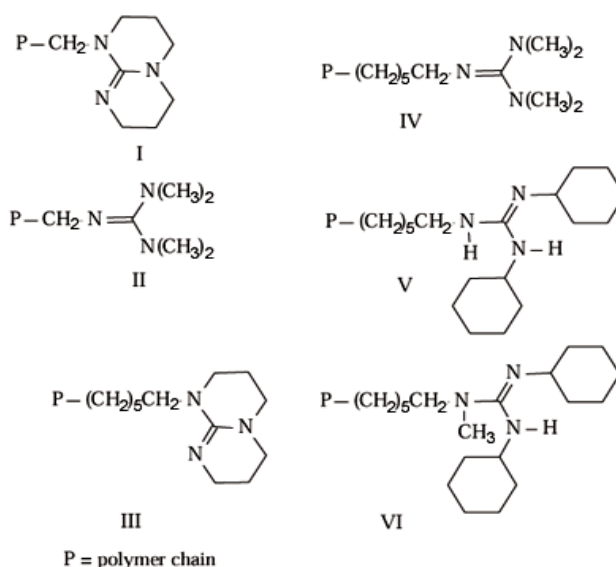
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Scheme 11. Heterogenization of guanidine on activated microcrystalline cellulose.

The catalytic performance of some alkylguanidines heterogenized on different substituted polystyrenes was investigated. The guanidine-containing polymers (Scheme 12) were used in the transesterification of soybean oil with methanol in several consecutive catalytic cycles.

The guanidines heterogenized on gel-type poly(styrene/divinylbenzene) with 1 meq Cl/g (polymers I and II) showed a slightly lower activity than their homogeneous analogues but allowed the same high conversions after prolonged reaction times. However, they slowly leached from the polymers, allowing only nine catalytic cycles. The guanidines heterogenized on linear polystyrene with the use of a 'spacer-arm' (polymers III, IV), were less active. Polymer V, which is symmetrically substituted showed an activity as high as polymer I. When another methyl group was introduced (polymer VI) its activity was slightly reduced. Furthermore, all polymers with a 'spacer-arm' suffered substitution reactions during the recycling experiments to form inactive hexasubstituted guanidinium compounds. A summary of the catalytic performance of these polymers is shown in Table 4.



Scheme 12. Molecular structures of some guanidine-containing polystyrenes.

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Table 4. Total turnover numbers and turnover frequencies (after 1 h) observed with guanidine-containing polymers in the transesterification of soybean oil with methanol.

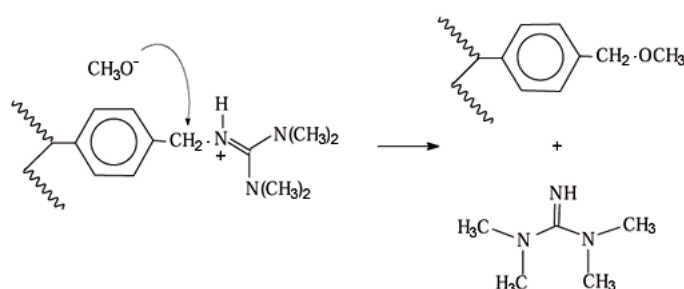
Catalyst	total turnover number ^{a,b} (number of cycles)	turnover frequency (h ⁻¹) ^c
I	124 (9)	15
II	118 (9)	12
III	36 (5)	13
IV	30 (4)	12
V	84 (6)	15
VI	42 (7)	14

a: turnover number: mol of products/ mol of catalyst.

b: conditions: 1 eq. of soybean oil, 6.9 eq. of methanol, 5 mol% of base, 70 °C. c: turnover frequency: turnover number/ reaction time.

The lower activity of the guanidine-containing polymers I and II, when compared to their homogeneous analogues, is probably due to the hydrophobicity of the polymer chain which reduces the concentration of the methanol at the active sites. However, at prolonged reaction times, the efficiency of the anchored catalysts is practically the same. The use of a 'spacer-arm' (polymers III-VI) was expected to improve the performance of the heterogenized catalyst. However, polymer IV showed the same activity as polymer II and polymer III was even less active than polymer I.

Despite less active than their homogeneous analogues, all polymer-containing guanidines could be reused in several consecutive reaction cycles. However, a loss of activity was observed, mainly due to leaching of the anchored base from the polymers, as mentioned above. Polymers I and II have the guanidine moiety bound to the benzylic CH₂ group of the polystyrene. After the protonation of the base, the electrophilic character of the methylene group is increased, thus becoming more susceptible to nucleophilic attack by methoxide ions present in the reaction medium. This attack results in the removal of the guanidine moiety from the polymer as shown in Scheme 13. The leaching of the guanidines from the other polymers follows a similar mechanism.



Scheme 13. Leaching of the guanidine moiety from the polymers.

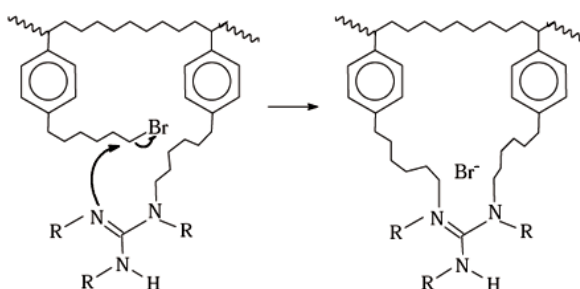
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For the polymers containing a 'spacer-arm', there is an additional factor that accelerates the deactivation of the supported catalysts. The anchored bases can react with electrophilic functional groups which are further away on the polymer chain, producing inactive hexasubstituted guanidinium compounds, as shown in Scheme 14. However, it is possible to deprotonate these hexasubstituted guanidinium compounds, which should give doubly anchored active guanidines whose leaching is less probable.



Scheme 14. Reaction of the heterogenized guanidines III-VI with unreacted 6-bromohexyl substituents.

ADVANTAGES OF BASE CATALYZED TRANSESTERIFICATION

Most popular of all method

- >90% of all bio diesel by this method
- Low temperature (150o F) and pressure (20 PSI)
- High conversion (>98%)
- Minimum side reactions
- Direct conversion- No intermediate step
- Ordinary material of construction

MATERIALS AND METHODS

EQUIPMENTS:

- Digital Weighing machine
- Flask
- Container water bath
- Thermometer
- Separation funnel
- Heating device

RAW MATERIALS:

Vegetable oil:

Diesel has a chain of 11-13 carbons and new vegetable oil has a chain of about 18 but wasted vegetable oil which is heated has chains of up to 32 carbons. To burn in an engine, the chain needs to be broken down to be similar in length to diesel.

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NaOH :

It is the catalyst for transesterification and works by cracking the vegetable oil molecules, splitting the triglyceride from the hydrocarbons and shortening the carbon chain.

Ethanol:

A little amount of ethanol is necessary in order to get the highest yield. If 90% yield is obtain that means 90% fatty acids have been eliminated from the vegetable oil. Generally 15% to 20% ethanol based upon the total weight of batch of oil is necessary.

Waste cooking oil :

The oil which is use in the restaurants, hotels, functions etc., is not reused. The reuse of fried oil is sometime toxic or causes illness to heath. Which leads to cancer etc., So these oil can be collected and be used for the production of biodiesel. And this diesel can be blended with convectional diesel.

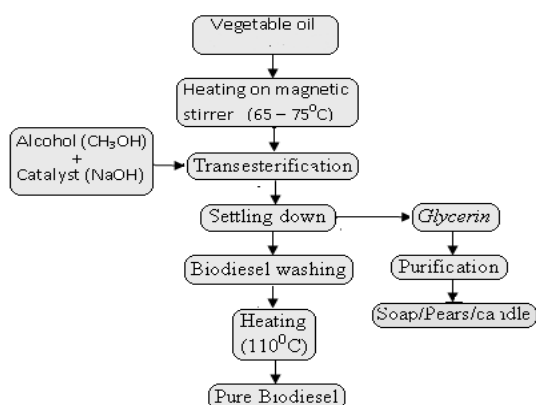
Experimental Procedure

The raw materials involved in the reaction are sunflower oil, palm oil, waste cooking oil, ethanol and the catalyst (NaOH). The different steps for the biodiesel production in laboratory are: Mixing of the ethanol and the catalyst in a flask. The moisture level should be kept as low as possible.

Water causes the formation of soap by saponification. It is necessary to reduce the formation of soap. Formation of soap consumes the catalyst is consumed and complicates the separation and purification process. Formation of soap also decreases the biodiesel yield.

The mix ethanol/NaOH is heated to 50°C (in a water bath) and stirred by a magnet at 800rpm (constant speed), until, the catalyst is completely dissolved in the ethanol. 200 ml sunflower, palm and its waste cooking oils is heated at 60°C. The solution ethanol-catalyst and the oil are mixed in a flask. The flask is introduced in a water bath at 50°C and stirred to 500 rpm. The reaction is performed during 60 minutes. The experiment is repeated a number of times varying the ratio of ethanol/oil and the catalyst weight.

FLOW SHEET OF PRODUCTION OF BIODISEL



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III. RESULT AND DISCUSSION

DETERMINING PHYSIOCHEMICAL PROPERTY

CALORIFIC VALUE

Calorific value of a fuel is the thermal energy released per unit quantity of fuel when the fuel is burned completely and the products of combustion are cooled back to the initial temperature of the combustible mixture. It measures the energy content in a fuel. The calorific value of vegetable oils and their methyl esters were measured in a bomb calorimeter

CETANE NUMBER

Measures the readiness of a fuel to auto-ignite. High cetane means the fuel will ignite quickly at the conditions in the engine (does not mean the fuel is highly flammable or explosive). Most fuels have cetane numbers between 40 and 60. Premium Diesel fuel typically has a cetane of 47.

DENSITY :

It is the mass per unit volume of any liquid at a given temperature. Density measurements were carried out using a pycnometer

FLASH AND FIRE POINT

A "flashpoint" is the temperature at which a fluid generates enough vapor to be ignited ("flash"). The fire point of a fuel is the temperature at which the vapour produced by that given fuel will continue to burn for at least 5 seconds after ignition by an open flame. These two parameters have great importance while determining the fire hazard (temperature at which fuel will give off inflammable vapour).

VISCOSITY:

It is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion.

Viscosity is measured using U-tube manometer

CLOUD AND POURPOINT

Cloud point: It refers to the temperature below which wax in diesel or biowax in biodiesels form a cloudy appearance. The presence of solidified waxes thickens the oil and clogs fuel filters and injectors in engines.

Pour point: The pour point of a liquid is the temperature at which it becomes semi solid and loses its flow characteristics.

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COMPARISON BETWEEN RAW DIESAL AND BIODIESAL

Physical Property	AS TM Standards	Diesel	Sun flower fresh Oil(bio diesel)	Sunflower Waste oil (biodiesel)	Palm oil (fresh oil (biodiesel))	Palm oil (waste oil) (biodiesel)
Density(g/cc)	800	826.5	911	875	890	8
Specific Gravity	0.8	0.8265	0.911	0.875	0.890	0.865
Viscosity	2.5-7.5	2.049	4.209	2.808	4.3	3.09
Cloud point			1	2	NA	NA
Pour point			0	1	NA	NA
Flash Point	Min ^o 38	78	58	62	53.09	56.9
Fire Point	Min ^o 42	82	63	65.09	58.43	60.87
Cetane	Min 45	47.73	49.78	46.73	58	52
Calorific Value (MJ/Kg)	Min 33	42.57	41.2	36	46.7	38

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IV. CONCLUSION

We observed that the efficiency of production of bio diesel from raw vegetable oil lesser than the waste cooking oil. Hence we are prefer waste cooking oils to be used for biodiesel production. It was observed that the degree of centralization of biodiesel plants influenced the impacts during the stages of transportation of the raw material, biodiesel processing and distribution of the product to the biodiesel stations. In this case, differences regarding the impact between raw vegetable oil and a waste cooking oil distribution will depend on various factors, like the area of the studied territory, the total production capacity or the homogeneity or heterogeneity of the distribution of crops and biodiesel stations. In general, in small territories centralized production was more suitable for the environment, decentralization being more advisable as the territory increased in area. For each of the cases analyzed, an optimum number of plants, which minimized the environmental impacts, was found. Being an alternative to waste management, processing of WCO into biodiesel has a positive contribution to the environment in the category of climate change. Again, the degree of centralization is a key point in order to determine the best environmental option, which is different for each case analyzed. The production of biodiesel from WCO is less harmful to the environment if it is performed with some degree of decentralization. This study illustrates the importance of considering the number of industrial plants in the production design, not only from an economic aspect but also from an environmental point of view.

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