

Optimization of Biodiesel Synthesis from Waste Cooking Oil Using a Heterogeneous Green Catalyst

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Abstract

The present study conducted investigations on Bd generated from palm WCO. In TE reaction, alkaline bases for catalysts are often employed. However, since WCO contains high Ct of free fatty acids, its direct use is not feasible, due to layer separation and saponification issues. A two-step process of esterification and TE was herein carried out. GC made from biomass was used. With lower Ct of WCO, maximum Bd yield was achieved using 5 wt.% from GC, CH₃OH:oil ratio of 12:1, reaction time of 70 min, T of 150 °C and stirring speed of 600 rpm. TE's second stage employed NaOH, T of 70 °C and Ct of 1.0 wt.%, for 70 min. Final yield was 95.65 wt.%. Most important variables determining economic feasibility were plant capacity and pricing of feedstock oil and Bd.

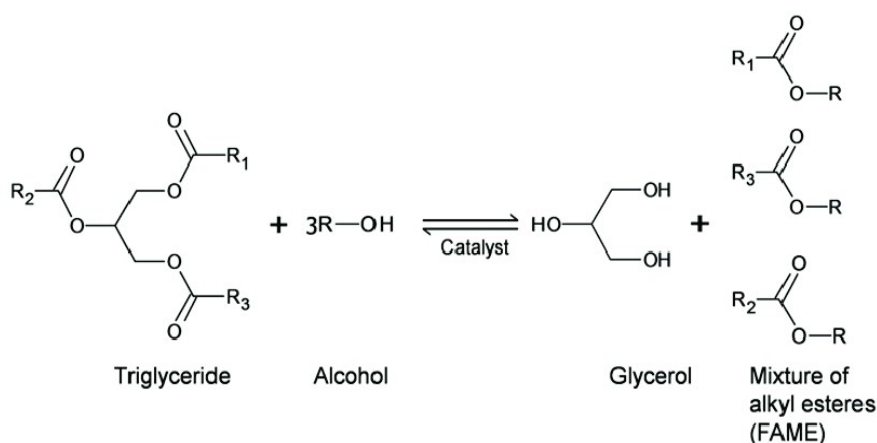
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Introduction*

Bd fuel, made from vegetable oil or animal fats, is a renewable domestic resource and clean-burning fuel that has a low environmental impact and is rapidly biodegradable, making it a better alternative to petroleum-based diesel. Several studies have been conducted on the usage of Bd as fuel. In Europe, it started to be commercially employed as a diesel alternative in the late 1980s. TE process of triacylglycerols occurs in vegetable oil or animal fats with an alcohol, while using an alkali or acid catalyst is currently the most popular approach to making Bd. Partially due to its affordability, CH₃OH is the most often employed alcohol in this methodology. Glycerin is a by-product of Bd from FAME. Due to its quick reaction

* The abbreviations list is in page 400.

time, alkali catalyzed TE has been widely used in the industry. Usual catalysts for alkalis are NaOH or KOH. Acid-catalyzed TE systems have been less researched than alkali ones. H₂SO₄ is often employed as a catalyst in acidic reactions. Researchers have concentrated on alternative fuel sources, due to growing concerns about global energy crises, and the impact of heavy fossil resource usage on global warming. Bio-based fuels (ethanol and Bd) are a resource that has received a lot of attention. According to a recent study on Bd's life cycle, its combinations with petroleum diesel significantly reduces GHG emissions [1, 2]. Grease, vegetable oils, animal fats and other materials are being used to make Bd. FAME is the main component of Bd molecule's chemical structure [3, 4]. The primary product of FAME is Bd, while the by-product is glycerin. Monoglycerides and diglycerides are the intermediates in this process [5]. The chemical equation in Fig. 1 depicts TE procedure.



R₁, R₂, R₃ = Hydrocarbon chain ranging from 15 to 21 carbon atoms

Figure 1: Bd synthesis by TE process from vegetable oils with CH₃OH [6].

Due to Bd beneficial characteristics, including its low S level and absence of phenolics, rubber and plastic, it has gained popularity for usage as a mixture ingredient, in any ratio, of petroleum-based fuel, and all major automakers have allowed its use. Bd does not need to be specially modified for usage in currently existing conventional compression ignition engines [7]. However, to discover a substitute catalyst with high activity, and to avoid the aforementioned drawbacks, one must take into account unfavorable characteristics of acids and bases. IL are a newly emerging class of chemicals that have shown some promise as GC, due to their advantageous features, including environmental friendliness, high thermal stability, negligible vapor pressure, non-flammability and adjustable physical and chemical properties [8]. GC have generated more interest than traditional catalysts, as they are clean and promising. Even though there are other IL, only GC are able to provide high yields for Bd manufacturing through TE process [9]. Due to their extraordinary capabilities, it will be fascinating to look into additional potential uses

of GC, and to investigate the impact of their various functional groups on Bd synthesis [10]. In this study, prepared BAIL was employed as GC, to esterify WCO for Bd production. The impact of various process factors on Bd production was investigated [11].

Experimental

Materials and methods

WCO was gathered from a nearby eatery. Purchased from Merck, employed chemicals included $C_4H_6N_2$, $C_7H_{12}N_2$, $C_8H_{15}N_2Cl$, H_2SO_4 , diethyl ether, toluene, acetonitrile, CH_3OH and KOH . None of these compounds underwent additional purification before use. According to ASTM and EN procedures, WCO's various physiochemical parameters, such as acid, peroxide, saponification and calorific values, kinematic viscosity, density, specific gravity, flash point and water content, were measured.

GC preparation

Two step catalytic process

Existing techniques described in literature were used to make BAIL with minimal modification. In a 250 mL flask equipped with a long condenser for reflux, starting materials, such as $C_8H_{15}N_2Cl$, $C_7H_{12}N_2$ or $C_4H_6N_2$, were separately dissolved in anhydrous acetonitrile, while being vigorously stirred, under N_2 purge. Then, while the mixture was still being continually stirred and turned cold, concentrated H_2SO_4 was gradually added. Continuous stirring was employed to guarantee that the reaction was completed. N_2 was utilized to flush HCl gas out of the reaction phase right away. BAIL was cleaned with toluene three times before being hoover dried for 8 h. Created BAIL were $BMIMHSO_4$, $BIMHSO_4$ and $MIMHSO_4$.

Esterification of WCO by IL (first stage)

Reduction of WCO acid value was this stage's goal. Prior to beginning esterification, WCO was heated in an oven, to remove any traces of moisture. A reflux condenser was placed on a heating plate with a determined amount of WCO. IL and a CH_3OH solution were made in the appropriate quantity and charged to WCO, while being continuously stirred. In order to provide and circulate cooled water for sustaining extremely heated CH_3OH during conversion process, the reflux condenser was built with a cooled water chiller. To investigate the impact of IL type on esterification process conversion percentage, the reaction was carried out under a variety of conditions. Reaction T, Ct from IL, stirring speed, $CH_3OH:WCO$ molar ratio and reaction time ranged from 80 to 180 °C, 3 to 7.5 wt/%, 100 to 700 rpm, 3:1 to 18:1, and 30 to 120 min, respectively. The three IL showed various patterns in the conversion of free fatty acids into esters. The mixture was placed into a separating funnel, once each reaction was finished, and it was kept overnight, to allow layers completely separation. After IL was separated, treated WCO was put through a TE reaction with an alkali GC.

Biomass-derived GC recovery

In the first phase of esterification, GC was recovered. Afterwards, CH₃OH was removed under vacuum, the mixture was briefly cooled, and it was centrifuged for 30 min, to separate IL from the treated WCO's bottom phase. GC was then cleaned with hexane and ethyl acetate, before being vacuum-dried, during 4 h, for its reuse.

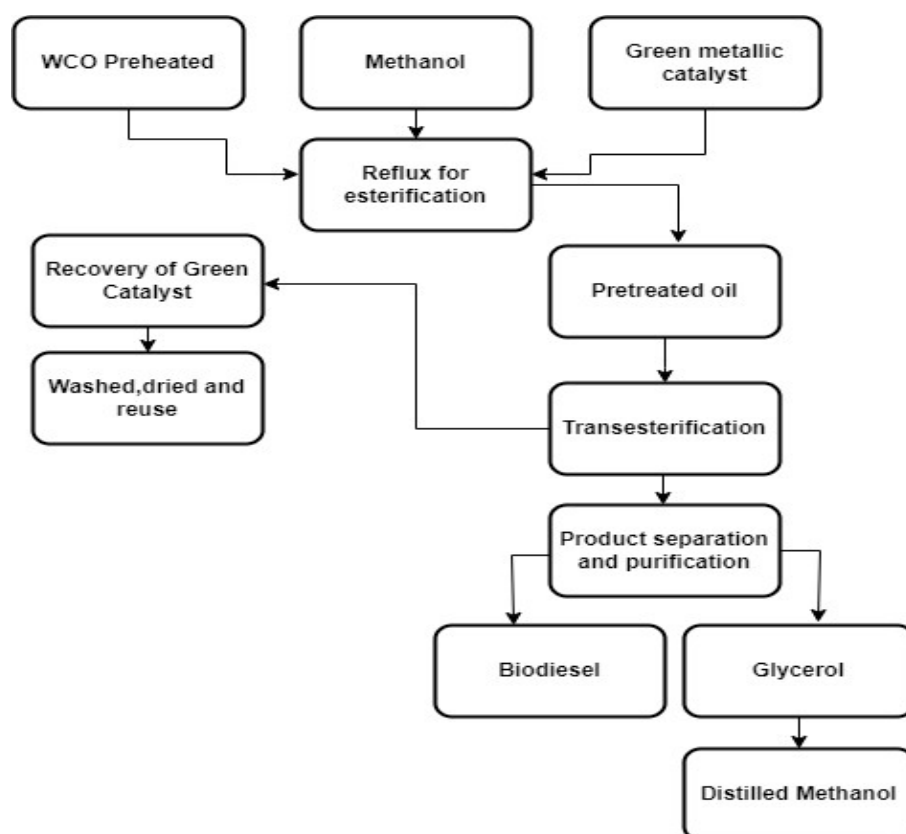


Figure 2: Flow sheet diagram, feedstock and GC preparation for Bd production.

Determination of yield

To compute Bd yield, after collection of its upper layer, it was calculated as the ratio of the final:initial oil weight. Bd gained 14 wt% for FAME generated WCO weight herein employed.

Results and discussion

Several WCO's similar physio-chemical characteristics were assessed using recognized techniques. Literature is sparse on the use of IL as GC for WCO-based Bd generation. BAIL utilized in this research were chosen and created as GC for the two-step process of producing Bd from WCO. To ascertain the ideal values for various reaction parameters, experiments were carried out above in a small scale setup. According to Fig. 2, a potential reaction pathway involving triglycerides, IL and CH₃OH was postulated.

GC recovery

The ability to recycle IL makes them a green solvent, among other things. To investigate the effectiveness of GC recovery, experiments for BMIMHSO₄ recycling were carried out. The resulting mixture divided into three layers after settling at room T; the top layer is made of Bd, the middle layer is made of glycerol, and the bottom layer is made of IL. For most time, IL layer was undetectable, because it is mixable with glycerol. This mixture was first centrifuged to separate it from Bd, and then the layers were separated. IL-containing bottom layer was taken apart and cleaned with hexane before being reused. The recycled GC was next charged with CH₃OH and then with WCO, to create Bd. The process was performed four times, until a small decline was noticed, as shown in Fig 3. The yield dropped to 81% when this GC was reused five times.

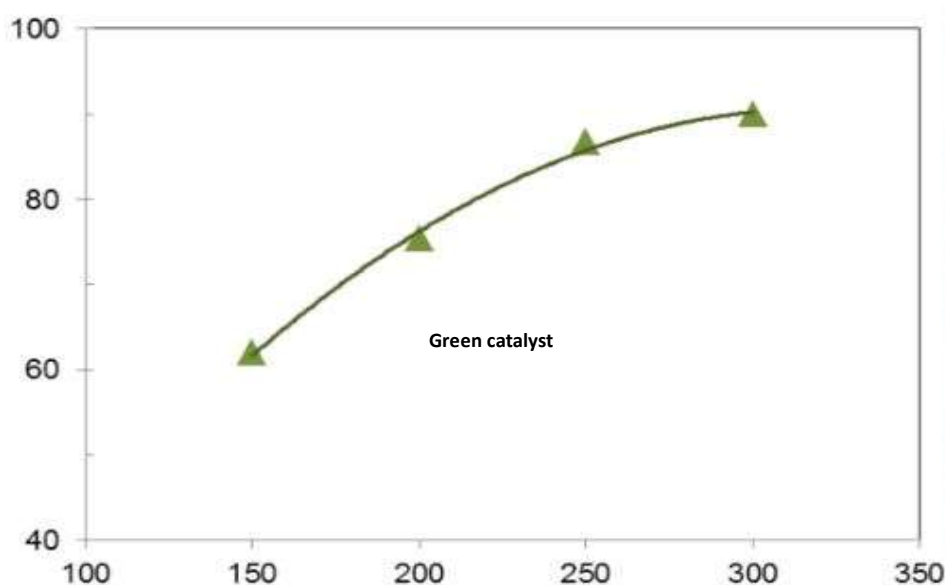


Figure 3: GC reusability vs. yield (%) of Bd.

Physical properties of Bd from WCO

The characteristics of Bd from WCO catalyzed by acidic IL met ASTM D-6751 and EN14214 standards I.

Conclusion

With a yield of up to 95%, the two-step conversion of WCO from palm trees into Bd has been effective. GC recovery and longer chain length, IL was chosen as the superior one. This result is consistent with earlier studies reported in the literature where it was shown that adding merely one, two extra atom of carbon to chain of alkyl could produce a similar result. Ct from GC was 5 wt/%, CH₃OH:WCO ratio was 10:1, reaction time was 70 min, T was 150 °C and stirring speed was 600 rpm.

Bd s output at ideal conditions was 95.65%. In addition to being environmentally beneficial, GC like Bd from inexpensive feedstock may have lower manufacture costs than those of traditional solvents. Future research needs to investigate the effect of increases in Bd yield on the environment.

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Conflict of interest

There is no conflict of interest associated with this research work declared by author.

Authors' contributions

M. Siddique: wrote paper. **A. Wakeel:** made flow chart. **M. Asif:** designed figures. **M. Laghari:** removed grammar mistakes. **S. K. Suri:** helped in references. **A. Munim:** removed plagerism. **N. Karamat:** set dois.

Abbreviations

ASTM: American Society for Testing and Materials

BAIL: Brønsted acid ionic liquid

Bd: biodiesel

BIMHSO₄: N-butylimidazolium hydrogen sulfate

BMIMHSO₄: 1-Butyl-3-methylimidazolium hydrogen sulfate

C₄H₆N₂: 1-methylimidazole

C₇H₁₂N₂: N-butyl-imidazole

C₈H₁₅N₂Cl: butyl-methyl-imidazolium chloride formula

CH₃OH: methanol

FAME: fatty acid methyl ester

GC: green catalyst

GHG: green-house gas

H₂SO₄: sulfuric acid

HCl: hydrochloric acid

IL: ionic liquid

KOH: potassium hydroxide

LW: lignocellulosic waste

MIMHSO₄: 1-methylimidazolium hydrogen sulfate

NaOH: sodium hydroxide

Rpm: rotation per minute

RSM: response surface methodology

T: temperature

TE: transesterification

WCO: waste cooking oil

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