Bio-Kerosene Production from *Jatropha Curcas* Seed: Characterization and Parameter Influence

.

ABSTRACT

Aim: To characterize and investigate parameter Influence of bio-kerosene produced from Jatropha Curcas Seed.
Study design: Oil extraction from the seeds of Jatropha Curcas and then transformation to produce bio-kerosene.
Place and Duration of Study: The study was conducted in the Department of Chemical Engineering, University of Lagos, Akoka, Lagos, Nigeria between June 2010 and November 2011. Further research study was done in the Department of Industrial Engineering, University of Alabama in Huntsville, Alabama, United States of America between August 2022 and April 2023.
Methodology: The raw jatropha curcas was converted oil into biofuel via a two-step method involving transesterification and pre-esterification operations. The free fatty acids (FFAs) was eliminated vai the reaction of methanol with the oil using an acid catalyst.The biodiesel yield was calculated using the already existing mathematical equation.
Results: Maximum biofuel yield of 94.5%was obtained from FFA 22.6% in the raw jatropha oil at optimum process parameters which arecatalyst concentration NaOH 1.0 wt%,methanol to oil molar ratio 4:1, reaction time 1.5 hours,reaction temperature at 318K and ultrasonic power 210W.
Conclusion: The biofuel physical properties prepared from jatropha oil with methanol were within the ASTM specified limits. However, there is need for strong international biofuel feedstock trading systems to enhance the existence of sustainable domestic biofuels industries. Also, government should pertake in significant roles in fostering biofuels industries development in the country. Competitive industries development will be aided by establishing regulatory mandates for commercial production of biofuel technology.

Keywords: Bio-Kerosene, Jatropha Curcas,Transesterification, Bio-oil Yield, Methanol/Oil ratio

1. INTRODUCTION

The improved and rising fossil-based fuels exploitation is a function of population expansion and economic and industrial growth which have also intensified environmental and energy problems thereby, becoming the main subject of discussion by humans presently. Various statistics have shown that natural gas, crude oil, coal and other fossil fuel derivatives take more than 80% of the total energy production on global basis. Agriculture, transportation and almost all industrial sectors rely on the usage of fuels obtained from non-renewable sources [1]. These fuels have been subjected to a severe reduction due to the continuous increasing societal energy demand coupled with greenhouse gas emissions generation that deteriorate ecosystems, affect climate change and cause potential risks to human health. Therefore, this has encouraged scientific community to look into finding alternative sources of sustainable, low-cost and renewable energy (e.g., hydraulic, wind, biomass and solar). Biomass obtained from agricultural, industrial and urban sources is a low-cost feedstock for chemicals and fuels production resulting from its non-edible nature, wide availability and carbon–neutral property. Biofuels have identified as one of the main sources of green energy and are effective substitutes for fossil fuels due to their environmental and economic and benefits [2]. Figure 1 represents different products obtained from biomass wastes and biorefinery processes while Figure 2 represents classification of biofuels and their generations.

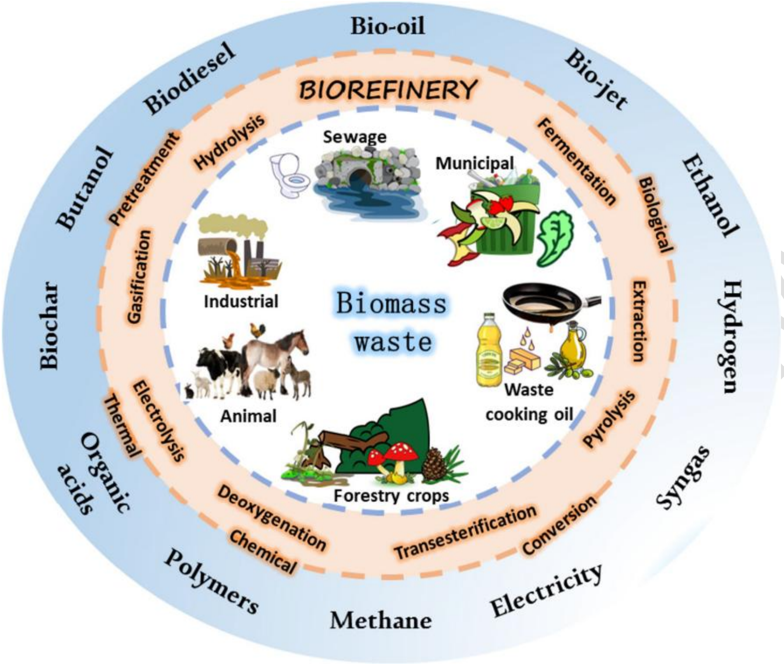
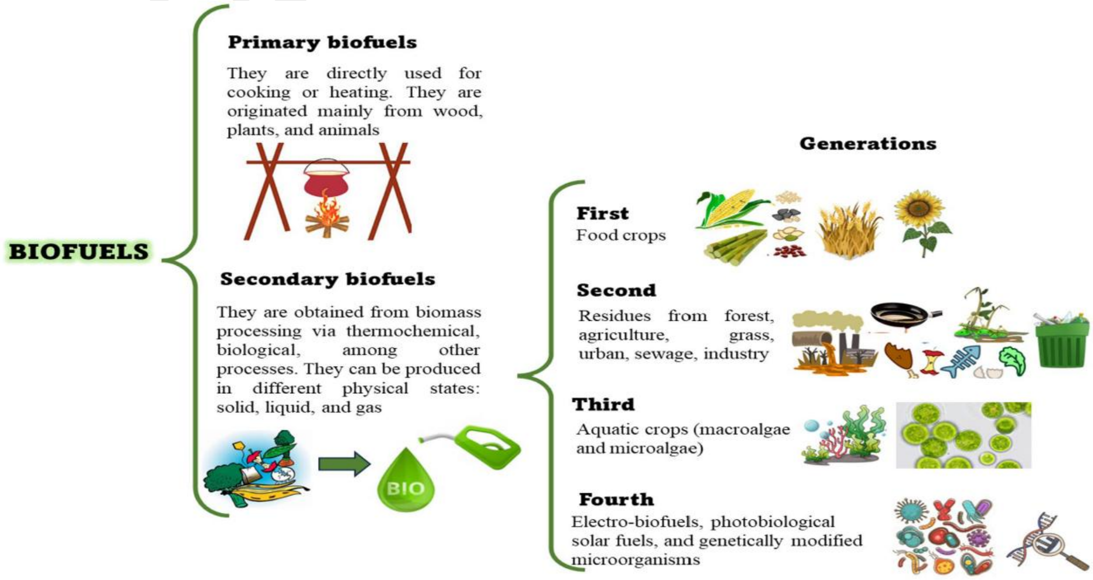


Figure 1: Different products obtained from biomass wastes and biorefinery processes [3]



They are directly used for cooking or heating. They are originated mainly from wood, plants, and animals

They are obtained from biomass processing via thermochemical, biological, among other processes. They can be produced in different physical states: solid, liquid, and gas

Residues from forest, agriculture, grass, urban, sewage, industry

Aquatic crops (macroalgae and microalgae)

Electro-biofuels, photobiological solar fuels, and genetically modified microorganisms

Figure 2: Classification of biofuels and their generations [4]

One of the technologically viable and ecofriendly promising alternative to fossil fuel kerosene fraction with long term efficiency is biokerosene.Edible biomass such as soybean oil, sunflower oil, rapeseed oil and coconut oil were utilized to make the the first biofuels generation. These are harvested products of agricultural practices and thus contest with global food requirements. The limited volume of farmland available has greatly restricted them from being used as long term transport fuel means. Thus, it is quite challenging to grow the required plants in order to meet the demand by both fuel and human. This may lead to high rise in the prices of edible oil and biofuels from these agricultural products. The competition between biofuel market and human consumption for these products may be high causing them to become more expensive. Environmental issues would possibly arise due to the deforestation of quite large number of plants producing the edible oil [3].

The aviation industry has been identified as one of the major contributors to greenhouse gas emissions. There is need for transition for the development and deployment of aviation biofuelsas a sustainable alternative. Particularly, there is an increasing movement to accept the use of cheap low-quality biomass wastes and feedstocks which could decrease the overall environmental impact and production cost [5]. Sustainable Aviation Fuels (SAFs) are interesting solution to decrease greenhouse gas emissions coming from the aviation industry. In the past, identified sources of biofuel production includes waste cooking oil and animal fats. Animal fat is infeasible because at room temperature,it turns into solid wax causing problems during the process of production. A mixture of vegetable and animal oils is the waste cooking oil which have pass throughphysical and chemical changes in the course of cooking. Waste cooking oil is adulterated by impurities of various kinds from the cooking process, such as free fatty acids and polymers. However, there are some drawbacks attached to these. In other to tackle these challenges, researchers are now looking into the production of bio-kerosene from non-edible oil. Example ofoil-producing non-edible plants are Pongamina Pinnata (Karanja), Jatropha Curcas (Jatropha), CalophyllumInophyllum (Polanga), Madhua Indica, Hevea Brasiliensis (Rubber) and many others [4].Jatropha stands out as the most beneficialamong these plants for the production of bio-kerosene based onsociological,economicaland environmental considerations. This study considered using Jatropha Curcas due to its low cost, non-edible and readily available attributes.

Jatropha Curcas belong to the family of Euphobiaceae. The name “jatropha”arose from the latin words jatros meaning “doctor” and trophe meaning “food”due to its numerous medicinal properties. The jatropha plant is natural to American tropics but grows naturally in subtropical and tropicalcountries such as India,sub-Sahara Africa, China and South East Asia. The seeds often mature in 3–4 months after flowering and continues to produce seeds for 50 years once it becomes an adult. Figure 3(a) and 3(b) represent the palnt and seeds of Jatropha Curcas respectively. About 40% of the seed content is the oil [6]. Table 1 presents the composition of the fatty acid content of the jatropha oil. The Jatropha oil can be extracted from the seeds bychemical, mechanical and enzymatic processes. Different methods have been established to transform vegetable oil such as jatropha oil into biofuel like biokerosene. The four main classes are involves using the vegetable oil directly, thermal cracking, micro-emulsion and transesterification [5].

(a) (b)

Figure 3: Jatropha Curcas (a) plant and (b) seeds

Table 1 - Composition of Jatropha Oil

Fatty Acid	Systemic Names	Structures	Composition (%)
Linoleic acid	Cis-9-cis-12-octadecadeneoic acid	$C_{18:2}$	35.3 – 42.1
Stearic acid	Octadecanoic	C_{18}	6.4 – 6.6
Palmitic acid	Hexadecanoic acid	C_{16}	13.4 – 15.3
Oleic acid	Cis-9-octadenoic acid	$C_{18:1}$	36.5 – 41.0
Other acid			0.8

It is highly imperative for SAFs to meet the specific properties of fuel in order to ascertain their successful integration. These properties include energy content for effective aircraft performance, density for optimumpayload capacity and fuel load, viscosity for smooth engine operation assurance, flash point for safe handling, freeze point for perfect operations in cold climate, low sulphur content to control emissions and specific distillation characteristics for it to be compatible with aircraft engines. Maintainance of these properties is important to produce SAFs that will strictly adhere to the operational safety and standards; and also contribute to a greener and more bearable future for aviation [7]. It is highly imperative to know the properties of the produced bio-kerosene and the effects the operating parameters have on the product quality. This study investigated the properties of bio-kerosene produced *Jatropha Curcas* and the process parameters influence on its quality.

2. MATERIAL AND METHODS

The raw jatropha curcaswas converted oil into biofuel via a two-step method involving transesterification and pre-esterification operations. The free fatty acids (FFAs) was eliminatedvai the reaction ofmethanol with the oil using an acid catalyst. Equation 1 best describes the process thus:

Equation 1

pre-esterificatin → purification → transesterification → phase separation

The reaction between methanol and raw oil was conducted after which a phase separation was executed in order to separate the acidic water from the gum impurities. Further reaction between the purified oil and methanol was conducted in the presence of an alkali catalyst. Finally, phase sepration between the biofuel product and the glycerol by-product was conducted. Influencing parametersaffecting the transesterification and pre-esterification processes were investigated.

Thejatrophaseeds were grinded until the required volmeof jatropha oil needed was obtained. Solid impurities were removed from the oil via filtration process to allow investigating the effects of water, FFAs and phospholipids effects on the reaction kinetics. After this, simulated oils was obtained via mixing different impurities with refined oil. The crude jatropha oil was also processed with NaOH solution to prepare the refined oil and active earth to eliminatemoisture and free fatty acid. The refined jatropha oil consisted ofwater < 0.1%, FFAs < 0.2 mg-KOH/g-oil and phospholipids < 0.04%. Oil samples having different water, FFAs and phospholipids contents were prepared through the addition of deionized water, oleic acid and soluble phospholipids into the refined jatropha curcas oil to allow investigating the influence of these factors on the pre-esterification step quantitatively. In the pre-esterification reactionstage, the solid acid catalyst used was made via calcining metatitanic acid. Analytical grade chemicals and reagents were used throughout the study.

2.1 SULFURIC ACID CATALYZED PRE-ESTERIFICATION PROCESS

Pre-esterification was executed inside a 250 ml three-neck flask. The flask was equipped with a reflux condenser anda mechanical agitator, and heated inside a water bath to adjust the temperature of the reaction. In the experiments, jatropha oil samples were placed in the flasks and heated up firstly to the intended temperature. After this, sulfuric acid and methanol were added into the mixture before tuning the agitator to the required speed and this indicated the starting of the esterification reaction. A tap funnel was used to separate the esterification products into layers. The obtained upper oil layer was then washed severally with water until the washing water pH was relatively 7.0. The final pre-esterified oil was then dried using anhydrous magnesium sulfate before subsequent transesterification.

2.2 SOLID ACID CATALYST PREPARATION AND ITS USAGE IN PRE-ESTERIFICATION PROCESS

The metatitanic acid, obtained from the commercial TiO_2 pigment process hydrolysis section, was a semi-finished product. It was a hydrolysis product which comprises oftitanium sulfates and adsorbed sulfuric acid without additional purification. The metatitanic acid sample was dried for 5 hourat 110◦C in the air and then sieved aftercrushing. The particles having a size lower than 125 µm were further calcined for the solid acid catalystpreparation. Pre-esterification occurred in the autoclave with aid of the solid acid catalyst. At the beginning, both the catalyst and the reactants were added, and the reactor was mechanically agitated at 1500 rpm and quickly heated at 7◦C/min.The reactor was slaked to stop the reactionafter the reaction is completed. The filtration of the slurry was conducted under vacuum and the liquid phases were permitted to settle in a tap funnel for the separation of the acidic water from the oil phase. The methanol and acidic water are the upper layer components[8]. The oil phase was received at the lower layer and was kept for 90 min at 110◦C in an oven in order to enable the evaporation of the methanol and the residual moisture. The feedstock for transesterification process was the obtained heated oil.

2.3 TRANSESTERIFICATION

Transesterification experiments were conducted using sodium hydroxide (NaOH) and potassium hydroxide (KOH) as the alkaline catalystunder atmospheric pressure. The process and the reactor were identical to those at pre-esterification. The products were glycerol and fatty acid ethyl esters. Water was used to thoroughly wash the fatty acid ethyl esters in order to eliminatecatalyst and soap before drying.Concentrated sulfuric acid was used as catalyst to perform an acid-esterification pretreatment. The flask with a water-cooled was filled with 40ml anhydrous methanol, 200ml jatropha oil and 4ml of sulfuric acid. The mixture was refluxed for 1hr at 318K in an ultrasonic reactor after rigorous stirring. After the reaction (stated as Equation 2), the filtration of the mixture was done and separation of the unreacted methanol from the liquid phase through rotary evaporation was conducted. Sodium chloride solution was used to wash the oil for three times and anhydrous sodium sulfate was subsequently used to dry it [9].The pretreated oil acid valuewas reduced after the pretreatment to only 0.7 mg KOH/g with 93.3% esterification rate.
Equation 2

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$$

The biofuel yield was calculated using Equation 3.

$$Biofuel\ yield\ (\%) = \frac{Total\ weight\ of\ methyl\ esters}{Total\ theoretical\ weight\ of\ methyl\ esters} \times 100 \quad \text{Equation 3}$$

Where the methyl esters total weight wasobtained from both steps while the total theoretical weight was calculated based on the assumption that 100% conversion of the fatty acids in jatropha oil occured. The procedure for the reaction is here stated. First, the dispersion of the catalyst in methanol via mechanical stirring at around 600 rpm was conducted. Then, the pretreated oil was added to the mixture and heated in a water bath to 318 K. After the reaction, distillation of the excess methanol under a vacuum condition was done while catalyst separation was conducted via the use of high-speed centrifugation method.Biofuel was then collected after the glycerol layer removaland then subjected to chromatographic analyses.

3. RESULTS AND DISCUSSION

3.1 QUALITY OF BIOFUEL FROM *Jatropha Curcas* OIL

The raw jatropha curcas liquid oils properties differ with respect to their diferent origins. The biofuel production process was affected by the presence of fatty acid in the crude jatropha curcas oil and also influence the properties of the fuel. Table 2 lists the quality of biofuel from jatropha oil to those of petro-fuel. They were prepared in The two-step process was used for the preparation under the described optimization conditions. The results revealed the conversionof the jatropha oils to biofuel (biodiesel and biokerosene) via the two-step process methodology adopted for the study. Significant decrease in the kinematic viscosity and acid value was observed with higher value in the flash point than those of the petro-fuelafter the transesterification and pre-esterification processes. The density, acid value, free glycerin, viscosityand flash point were in accordance with the ASTM D6751 biofuel standards. Primarily, the biofuel acid value strongly indicates the presence of FFA [10]. An acid value that is more than 0.8 mg-KOH/g is an indication that the fuel system deposits can cause reduced life of filters and fuel pumps. A fuel with higher viscosity value can lead into poor fuel combustion causing deposit formation. The fatty acid ethyl esters flash point is much morethan that of petro-fuel which can cause improved fire safety. The free glycerin number is a measurement of the by-product glycerin volumepresent in the biofuel.

Table 2 –Biofuel quality from jatropha curcas oil

Property	**Acid Value (mg-KOH/g-Oil)**	**Density (g/ml)**	**Kinetic Viscosity (mm^2/s)**	**Glycerol Content (%)**	**Flash Point (^{o}C)**
Sample 1, Oil	10.1	0.9160	36.8	-	-
Sample 1, FAMA	0.29	0.8810	5.13	0.02	164
Sample 2, Oil	2.80	0.9176	33.49	-	-
Sample 2, FAMA	0.18	0.8764	4.06	0.02	166
ASTM D6751	<0.8	0.82-0.90	1.9-6.0	≤0.02	≥130

3.2 INFLUENCE OF REACTION PARAMETERS ON BIOFUEL YIELD

A two-step process was adopted for the biofuel production involving the jatropha oil pretreatment (acid-esterification) and solid base catalytic transesterification experiments as first and second steps respectively. The transesterification process involved three consecutive reversible reactios in which the jatropha oil was uninterruptedly converted into monoglyceride and diglyceride and then finally into fatty acid methyl esters and glycerin. The parameters considered for the study were varied for each ot the experiments.

3.2.1 Methanol-to-Oil Molar Ratio

The methanol/jatropha-oil molar ratio was an important factor affecting methyl esters yield. For each mole of the jatropha oil, 3 mol of methanol was stoichiometrically required. However, in practice, methanol/oil molar ratio should be more than the stoichiometry value so as to enhance driving the reaction towards completion to produce extra methyl esters. The methanol/jatropha-oil molar ratio influence on the biofuel yield was examined and an increase in the methyl esters yield from 63.0 to 94.7% was noticed when the ratio was increased from 3/1 to 4/1. Because of the immisicibility nature of jatropha oil with methanol, incomplete reaction was observed which was limited by thermodynamic and diffusion processes. Thus, it is necessary to apply excessive methanol during the reaction in order to promote the reaction. When the molar ratio was relativel close to 4/1, maximum yield of 94.7% was attained. A high esters rate of formation was due to the higher molar ratio over the stoichiometric value and could ascertain complete reaction [11]. However, it was observed that excessive methanol had no significant influence on the yield at molar ratios more than 4/1. Conversely, more time was needed for the subsequent separation stage to occur due to the difficulty of the separation of the esters layer from glycerol as a result of methanol having one polar hydroxyl group which could emulsify the products. Thus, 4/1 was picked as the best methanol/oil molar ratio for the study.

3.2.2 Catalyst Dosage

The influence of the mass of NaOH/KOH catalyst reflected high activity because they have large surface area and strong basic sites. Catalyst concentration strongly influenced the transesterification reaction. In the absence of catalyst, little reaction happened. The catalyst concentration influence on the biofuel yield was exmined. The yield of was esters increased from 53.8% to the maximum value of 93.9%when the concentration of the catalyst was increased from 0.5 to 1.0 wt% . This was due to the fact that the catalyst concentration increased from 0.5 to 1.0 wt% as a result of increase in contact between the catalyst and reactants. However, a drop in biofuel yield was experienced when the catalyst concentration was increased further beyind 1.0 wt%. This observation could be attributed to a mixing problem involving products, reactants and catalyst [12]. Additionally, ease of transesterification process emulsification was observedin the presence of excess catalyst and led into hard products separation. So the optimized catalyst concentration was 1.0 wt%.

3.2.3 Reaction Temperature

Anotherimportant factor which influences the yield of biofuel is the reaction temperature.Each experiment was conducted for 1.5 hours using4/1 methanol/oil molar ratio and 1 wt% catalyst. The results revealedthat at low temperatures, the yield of biofuel was low with only 52.4% yield for 1.5 hours at 303 K. Biofuel yield increased severely as temperature rose, and attained 94.2% at 318 K. However, decrease in the biofuel yieldwas observed with further increase in temperature. At higher temperature than 318 K, vaporization of methanol would occurfollowed by thebubbles formation, which could hinder reactions on the three-phase interface [13]. Therefore, the optimized temperature was around 318 K.

3.2.4 Ultrasonic Power

The ultrasonic power effect on the yield of biofuel was examined using1 wt% catalyst, methanol/Jatropha-oil molar ratio of 4/1 and temperature of 318K. The yield of biofuel increased from 77.7% to 94.5% when the ultrasonic power was increased from 180 to 210 W. A three-phase reaction mixture was formed by methanol, jatropha oil and solid catalyst during the production of biofueldue to their immiscibility. Ultrasonic irradiation enhanced sufficient mixing, assited the formation and breakage of micro-scale bubbles to create local high pressure and temperature, and also provided alternative energy source to stimulate reactions. However, a futher increase in the ultrasonic power from 210 to 270W reduced the biofuel yield from 94.5 to 76.9%. The was due to the vapourization of methanol leading to fog formation on the liquid surface at higher ultrasonic power [15].

Three repeated tests were conducted at the optimized condition (catalyst concentration of 1.0 w t%,methanol/oil molar ratio of 4/1, reaction temperature of 318 K and ultrasonic power of 210 W) and an average biofuel yield of 95.2 ± 0.6% was obtained in 1.5 hours. The yield (95.2%) was more than the previous reported works conducted at severer reaction conditions. The possible reason for the high conversion rate is due to ultrasonic radiation which enhances thereactants mixing with catalyst and promotes reactions, and the highly active catalysts [16].

4. CONCLUSION

The properties such as kinematic viscosity, acid value, flash point and density obtained from literature are roughlyequal to those from local jatropha oil chemical analysis. The jatropha curcas oil was prepared via a two-step process with methanol. It was observed that the maximum yield of biofuel of 94.5%was obtained from FFA of 22.6% in raw jatropha oil by using the optimum process parameters such as catalyst concentration NaOH 1.0 wt%, methanol to oil molar ratio 4:1, reaction time 1.5 hours,reaction temperature at 318K and ultrasonic power 210W. The physical properties of biofuel from jatropha oil with methanol were observed to be within the ASTM specified limits. However, in order to have sustainable domestic biofuels industries, establishment of strong international biofuel feedstock trading systems is important. Also, government should pertake insignificant roles in fostering biofuels industries development in the country. Competitive industries development will be aided by establishing regulatory mandates for commercial production of biofuel technology.

REFERENCES

1. Wei W, Wu J, Shao Q, Yu Z, Yu H, Zhao G. Biodiesel production using a biomass-based solid acid catalyst synthesized from agricultural residue garlic peel. Waste Biomass Valor. 2022; 13:3597–3609.

2. Why E, Ong H, Lee H, Chen W, Asikin-Mijan N, Varman M. Conversion of bio-jet fuel from palm kernel oil and its blending effect with jet A-1 fuel. Energy Convers Manage. 2021; 243:114311.

3. Wu Y, Wang Z, Ma X, Xue C. High temperature simultaneous saccharification and fermentation of corn stover for efficient butanol production by a thermotolerant Clostridium acetobutylicum. Process Biochem. 2021; 100:20–25

4. Oehmichen K, Majer S, Müller-Langer F, Thrän D. Comprehensive LCA of Biobased Sustainable Aviation Fuels and JET A-1 Multiblend. Appl. Sci. 2022; 12, 3372.

5. Yoo E, Lee U, Wang M. Life-Cycle Greenhouse Gas Emissions of Sustainable Aviation Fuel through a Net-Zero Carbon BiofuelPlant Design. ACS Sustain. Chem. Eng. 2022; 10, 8725–8732.

6. Liu YY, Lu HF, Liang B, Chen P. Pre-esterification of Jatropha curcas L. seed oil for Biodiesel Production. China Oils & Fats. 2007; 32, 43–46.

7. Goswami L, Kayalvizhi R, Dikshit PK, Sherpa KC, Roy S, Kushwaha A, Kim BS, Banerjee R, Jacob S, Rajak RC. A critical review on prospects of bio-refinery products from second and third generation biomasses. Chem Eng J. 2022; 448:137677. https:// doi. org/ 10. 1016/j. cej. 2022. 137677

8. Gouran A, Aghel B, Nasirmanesh F. Biodiesel production from waste cooking oil using wheat bran ash as a sustainable biomass. Fuel. 2021; 295:12054. https:// doi. org/ 10. 1016/j. fuel. 2021. 120542

9. Gousi M, Andriopoulou C, Bourikas K, Ladas S, Sotiriou M, Kordulis C, Lycourghioti A. Green diesel production over nickelalumina co-precipitated catalysts. Appl Catal. 2017; 536:45–56. https://doi. org/ 10. 1016/j. apcata. 2017. 02. 010

10. Gousi M, Kordouli E, Bourikas K, Symianakis E, Ladas S, Kordulis C, Lycourghiotis A. Green diesel production over nickelalumina nanostructured catalysts promoted by copper. Energies. 2020; 13(14):3707. https:// doi. org/ 10. 3390/ en131 4707

11. Abhishek S. Biodiesel Production through Ultrasonic Cavitation Process and Performance Testing. M. Eng Thesis, Department of Mechanical Engineering, Delhi College of Engineering, University of Delhi, 2009.

12. Cheng SF, Choo YM Kinetic Study on Transesterification of Jathropha Curcas. Journal of Jatropha Curcas Research. 2019; Vol. 16 (2), 23, 33, 26. Pages 1091-1096

13. Xiong M, Huang J, He X, Zhou Z, Qu X, Faisal S, Abomohra A. Evaluation of bio-oil/biodiesel production from co-pyrolysis of corn straw and natural hair: a new insight towards energy recovery and waste biorefinery. Fuel. 2023; 331:125710. https:// doi. org/ 10. 1016/j.fuel. 2022. 125710

14. Xue X, Liu J, Xia D, Liang J. Hydrocarbon-rich bio-oil production from the coupling formaldehyde-pretreatment and catalytic pyrolysis of poplar sawdust. Biomass Bioenergy. 2023; 173:106807. https:// doi.org/ 10. 1016/j. biomb ioe. 2023. 106807

15. Devanesan MG, Viruthagiri T, Sugumar N. Transesterification of Jatropha Oil using catalytic and non-catalytic approaches Journal of Biotechnology. 2007; vol 6(21) page 2497-2501.

16. Dijkstra AJ. Some Thoughts on the Mechanism of Ester Interchange Reactions Involving Acylglycerols. European Journal of Lipid Science and Technology. 2020; 122(10): p. 2000188.