Jatropha Bio-Diesel Production Technologies

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Abstract—The interest in using Jatropha curcas L. (JCL) as a feedstock for the production of bio-diesel is rapidly growing. The properties of the crop and its oil have persuaded investors and policy makers consider JCL as a substitute for fossil fuels to reduce greenhouse gas emissions.

In this paper, we give an overview of the currently available information on the different process steps of the production process of bio-diesel from JCL. Based on this collection of data and information the best available practice, the shortcomings and the potential environmental risks and benefits are discussed for each production step. The paper concludes with a call for general precaution and for science to be applied.

Index Terms—Jatropha–bio-diesel–greenhouse, gas, emissions-wasteland, reclamation.

I. INTRODUCTION

With the ever-increasing demand for energy, coupled with the dwindling supplies of fossil fuels, the world has to look for other prospective sources of energy which could complement standing depletable fossil fuel sources and / or eventually replace them [1].Many research organizations around the world have been studying and developing various technologies for the use of new and renewables energy sources [2].

Research activities around the world have come to the conclusion that biomass is presently the only available renewable option to produce transport fuels which are carbon neutral and can be stored and transported in large quantities using available petroleum infrastructure[2]-[4].

Biomass is already used to produce liquid transportation fuels namely, bioethanol and biodiesel from farm human feed products[2].Yet, the trend nowadays, is to develop production technologies for both products, from agricultural wastes and non-edible seed oils[4].

Under Egypt's land and water supply availabilities only non-edible oils such as Jatropha, Jojoba and castor oils can be considered for biodiesel production. Their plants can be grown on a large scale on non-cropped marginal land and wastelands.

In this paper, we present a state of the art literature review of the whole Jatropha bio-diesel production process. This collection of data and information enables us to discuss the actual best practices for production of Jatropha bio-diesel

II. JCL CHEMISTRY AND ANALYSIS

High-energy density liquid components, which can be used to make liquid fuels, are produced in plants as triglycerides, or terpenes [1]-[4].Triglycerides, as fats and oils, are found in the plant and animal kingdom and cosist of water-insoluble, hydrophobic substance that are made of one mole of glycerol and three moles of fatty acids[5]-[12].

Typically 1% of the vegetable oils is made up of unsaponifiable compounds (carotenoids, phosphor lipids, tocophenols or tocotrienols and oxydation products) [12].

The composition and characteristics of the crude Jatropha CL (JCL) oil are shown in Table I.

TABLE I: JCL OIL COMPOSITION AND CHARACTERISTICS [12]

	Range	Mean	S.D.	n				
Specific gravity (gcm ⁻³)	0.860-0,933	0.914	0.018	13				
Calorific value (MJkg ⁻¹)	37.83-42.05	39.63	1.52	9				
Pour point (°C)	-3			2				
Cloud point (°C)	2			1				
Flash point (°C)	210-240	235	11	7				
Cetane value	38.0-51.0	46.3	6.2	4				
Saponification number (mgg ⁻¹)	102.9-209.0	182.8	34.3	8				
Viscosity at 30°C (cSt)	37.00-54.80	46.82	7.24	7				
Free fatty acids % (kg kg ⁻¹ *100)	0.18-3.40	2.18	1.46	4				
Unsaponifiable % (kg kg ⁻¹ *100)	0.79-3.80	2.03	1.57	5				
Iodine number (mg iodine g ⁻¹)	92-112	101	7	8				
Acid number (mg KOH g ⁻¹)	0.92-6.16	3.71	2.17	4				
Monoglycerides % (kg kg ⁻¹ *100)	Nd-1.7			1				
Diglycerides% (kg kg ⁻¹ *100)	2.50-2.70			2				
Triglycerides % (kg kg ⁻¹ *100)	88.20-97.30			2				
Carbon residue% (kg kg ⁻¹ *100)	0.07-0.64	0.38	0.29	3				
Sulfur content % (kg kg ⁻¹ *100)	0-0.13			2				
S D-standard deviation: $n = number of observation used: nd = no data$								

S.D=standard deviation; n = number of observation used; nd = no data

We can note from Table I that the values of free fatty acid (FFAs), un- saponifiables, acid number and carbon residue figures show a very wide range, a fact which indicates that the oil quality is dependent on the interaction of environment and genetics. These wide ranges should be taken into consideration with regard to further processing of the oil.

It is important to point out that pure vegetable oils (VOs) can not be used directly in diesel engines because of the high viscosity, low volatility, and engine problems including coking on the injectors, carbon deposits, oil ring sticking, and thickening of the lubricating oils [4], [12].Yet, they can be used as base for liquid engine fuels in various ways, e.g. blends with other components, micro-emulsification, transesterification (TE), and hydrotreating [4].

III. BIODIESEL PRODUCTION TECHNOLOGIES

A. Homogeneous Catalysts for the Transesterification of Vegetable Oil [8]-[15]: Transesterification Chemistry Transesterification (called alcoholysis as well) of vegetable oils is the reaction of the oil constituents (triglycerides) with excess methyl or ethyl alcohol, in a three-step reaction as follows:

$$MG+M$$
 \longleftarrow $G+E$

 $TG + M \longrightarrow DG + E$ $DG + M \longrightarrow MG + E$

where TG,DG,MG are respectively the tri-,di-, and mono glycosides, and M,G, and E indicate methanol, glycerol, and the mixture of methyl esters which form biodiesel.



Fig.1. Flow diagrams comparing biodiesel production using the alkali-(a) and lipase-catalysis (b) processes [20].

All the reaction steps are reversible, hence the need to use high excess of alcohol, and a catalyst mostly a base e.g. Na OH, KOH, and their alkoxides.

It has been demonstrated that the methanol - oil molar ratio, catalyst concentration, and reaction temperature are the significant parameters affecting the yield of FAME (Fatty acid methyl ester).

Alkali- catalyzed TE proceeds ≈ 4000 times faster than that catalyzed by the same amount of an acidic catalyst.

Methanol or ethanol are the main alcohols used for the VO^s TE. Methanol is commercially available in an hydrous form, and the catalyst (sodium hydroxide) dissolves quickly in methanol.

Potassium hydroxide is used as catalyst when ethyl alcohol is used for TE due to it's higher solubility in ethanol.

However, producing Fatty acid ethyl ester (FAEE) is of high interest because it yields an entirely agricultural-based fuel, besides the energy content and cetane number are higher.

Optimum molar ratio of alcohol/ oil is 6/1 in the case of

methanol, and 12/1 for ethanol.

For TE of JC, catalyst requirement is ≈ 1 wt% of the oil, and the reaction is conducted close to the boiling point of methanol (60-70°C).

The products of the reaction are in two phases: a glycerol – rich phase and a methyl ester- rich phase. These two phases are physically separated, and treated to produce ASTM standard Biodiesel, and pure glycerin.

The optimum combination for reducing the FFA[§] content in Jatrapha oil from 14% to less than 1% was found to be 1.43% H₂SO₄ acid as catalyst, 0.28 V/V methanol- to-oil ratio, and 88 min. reaction time at a temp. of 60 °C, as compared to a 5/1 molar ratio methanol- to- oil, and 24 min. reaction time at a temp. of 60 °C for producing biodeisel, using 0.55% W/V KOH as an alkaline catalyst.

B. Heterogeneous Catalysts for the Transesterification of Vegetable Oils [16]

Despite industrial applicability, homogeneous catalysts have their limitations: the catalyst dissolves fully in the

glycerin layer, and partially in the FAME layer, which makes the product separation arduous. As a result, biodiesel should be cleaned through a slow, tedious and environmentally unfriendly water washing process to remove excess catalyst. Moreover, catalyst- contaminated glycerin is becoming a disposal problem. Another negative aspect is that the catalysts are non-reusable [17]-[19].

These problems have initiated research work and development of heterogeneous catalysts which can be easily removed from the product and recycled [16]-[19].

Yet, current heterogeneous catalysts pose their own problems, namely, they are not as active as homogeneous catalysts, and they require higher reaction temp^{\pm} (200-250°C) and pressures [13].

Furthermore, it should be taken into consideration that the presence of FFA^s in the feed will strongly poison solid base catalysts. In case of acidic catalysts, strong deactivation occurred when the catalyst was reused [10].

Although most of the reported work in the field of TE using heterogeneous catalysts deal with research and development studies, yet, it is worth mentioning that a 160,000 T/y commercial plant, using the Hester tip-H technology developed by the IFP, has started production since 2006. The catalyst is a mixed oxide of zinc and aluminium, the operating temperature is 200-250 °C, and a pressure of 50 atmosphere[18].

C. Enzymatic TE of Vegetable Oils [20].

Lipase enzymatic catalysts, can catalyze estrification and trans-esterification reactions. The advantages of lipase catalysts are their ability to catalyze both TE and E of FFA^s_{in} one_step, production of glycerol side-stream with minimal water content and little or no inorganic material, and recyclability, as could be noted from the diagrams for biodiesel production by the alkali and lipase catalysis (Fig1).

It is interesting to note that Jatropha seeds are reported to contain lipase activity which could also catalyze TE reactions. However, enzymatic catalysts have high costs, and deactivate due to feed impurities.

D. Non-Catalytic Super Critical Vegetable Oils Conversion to FAME "Fig. 2" [21].

With the aim of developing a novel methanolysis process for vegetable oils without using any catalyst, it has been demonstrated that preheating to a temp_s of 350° C, and 100-250 atm. and treatment for 240 s in supercritical methanol are sufficient to convert vegetable oils to FAME[§] with a higher yield than that obtained by alkali catalysts. Since Supercritical methanol has a hydrophobic nature with a lower dielectric constant, non-polar TG[§] can be well solvated with supercritical methanol to form a single phase oil/ methanol mixture. Free fatty acids (FFA^S) contained in the vegetable oils could also be converted efficiently to FAME in supercritical methanol, leading to increase of the total yield of FAME[§].

The purification of products after TE reaction is much simpler and more environmentally friendly compared with the alkali catalyzed method. However, the supercritical method requires higher temperatures and pressures, and large amounts of methanol.

Reaction with SC methanol has the following advantages:

- 1) $TG^{\underline{S}}$ and $FFA^{\underline{S}}$ are reacted with equivalent rate.
- 2) The homogenous phase eliminates diffusive problems.
- 3) The process tolerates great percentages of water in the feedstock.
- 4) The catalyst removal step is eliminated.



IV. JCL FATTY ACID METHYL ESTER EVALUATION AND PERFORMANCE

Stability, poor low temperature properties, and a slight increase in nitrogen oxides (NOx) exhaust emissions [21]. Ethyl and isopropyl esters have improved low temperature properties without comprising cetane number or oxidation stability [21].

A. Characteristics and Composition [12].

Various specifications for FAMEs such as ASTM-D6751 and EN 14214 are presented in Table II together with JCLFAME characteristics. It is clear that JCL FAMEs comply with these specifications.

Yet, there are some technical problems with biodiesel which have persisted to the present time, namely, oxidation

B. Performance

More than 100 years ago, Dr. Rudolf Diesel invented the original diesel engine and designed it to run on a host of fuels including heavy mineral oil, and vegetable oils. His first experiments were catastrophic failures, but by time he showed his engine at the World Exhibition in Paris in 1900and it was running on 100% peanut oil.

Using biodiesel in a convential diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulphates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. Neat biodiesel reduces CO₂ emissions by more than 75% over petroleum diesel [21].

The use of biodiesel decreases the solid carbon fraction of particulate matter since the oxygen in biodiesel enables more complete combustion to CO_2 , and reduces the sulphate fraction. Emissions of nitrogen oxides (NO_x) increases with

the concentration of biodesel in the fuel. Some additives have shown promise in modifying the increase [22].

TABLE II: JCL (M) ETHYL ESTER COMPOSITIO AND CHARACTERISTICS WITH THE CORRESPONDING VALUES OF THE EUROPEAN (EN 14214:2003), GERMAN
(DIN V 51606) AND THE USA STANDARDS (ASTM D 6751)

	(BIII 1 01000)	inter inn e	DI I D III (D	mabb	(110 1111 1	3 0/01)			
	JME			JEE n =1	EN 14214:203	DIN V 51606	ASTM D6751		
	Range	Mean	S.D	n					
Density (gcm ⁻³)	0.864-0.880	0.875	0.007	6	0.89	0.86-0.90	0.87-0.90		
Calorific value (MJ kg-1)	38.45-41.00	39.65	1.28	3					
Flash point (°C)	186	186	11	4	190	min 120	min 110	min 130	
Cetane value	50.0-56.1	52.3	2.3	5	59	min 51	min 49	min 47	
Saponification number (mgg ⁻¹)	202.6			1					
Viscosity at 30°C (cSt)	4.84-5.65	5.11	0.47	3	5.54	3.5-5.0	3.5-5.0	1.9-6.0	
Iodine number (mg iodine g^{-1})	93-106			2		Max 120	Max 115	Max 115	
Acid number (mg KOH g ⁻¹)	0.06-0.5	0.27	0.22	3	0.08	Max 0.5	Max 0.5	Max 0.5	
Monoglycerides %(kg kg ⁻¹ *100)	00.24			1	0.55	Max 0.8	Max 0.8		
Diglycerides %(kg kg ⁻¹ *100)	0.07			1	0.19	Max 0.2	Max 0.4		
Triglycerides %(kg kg ⁻¹ *100)	nd			0	nd	Max 0.02	Max 0.4		
Carbon residue %(kg kg ⁻¹ *100)	0.02-0.50	0.18	0.27	3		Max 0.3	Max 0.3	Max 0.5	
Sulfur content %(kg kg ⁻¹ *100)	0.0036			1		Max 0.01	Max 0.01	Max 0.015 ^a	
Sulfur ash %(kg kg ⁻¹ *100)	0.005-0.010	0.013	0.002.	4		Max 0.2	Max 0.03	Max 0.02	
(M)ethyl ester content %(kg kg 1 *100)	99.6			1	99.3	min 96.5			
Methanol %(kg kg ⁻¹ *100)	0.06-0.09			2	0.05	Max 0.2	Max 0.3		
Water % (kg kg $^{-1}$ *100)	0.07-0.01			1	0.16	Max 0.5	Max 0.3	Max 0.5	
Free glycerol %(kg kg ⁻¹ *100)	0.015-0.030			2	nd.	Max 0.02	Max 0.02	Max 0.02	
Total glycerol %(kg kg ⁻¹ *100)	0.088-0.100			2	0.17	Max 0.25	Max 0.25	Max0. 24	
S.D. = standard deviation : $n = number of observations used; nd = no data.$									

a Maximurr 0.015% for S 15 Grade and maximum 0.05% for S 500 Grade.

Ref. Biomass and Bioenergy 32 (2008) 1063-1084 [12].

V. CONCLUSIONS

A. JCL Oil Chemistry

Some of the properties of JCL oils produced from different species are more or less the same, while others are widely variable. The $FFA^{\underline{S}}$ content of the oil is one of the variable properties which should be given paramount retention, since it decides the FAME production scheme and the economics of the process.

B. JCL FAMES Production

At present, the most widely used technology for FAME production is the homogeneous alkali catalysed process. Yet, from between the technologies under development and those which have entered commercial application, two new technologies, namely, the super critical (SC) non-catalytic TE, and the newly developed heterogeneous solid catalyst process, capture interest.

Yet, the SC transesterification process has been in commercial application, mainly in Germany, long before the introduction of the heterogeneous solid catalyst technology.

REFERENCES

- [1] P. K. Asiri *et al.*, "Survey of oils for use as diesel fuels," *JAOCS*, vol. 73, no. 4, pp. 470-474, 1996.
- [2] G. M. Gibtz *et al.*, "Exploitation of the tropical oil seed plant Jatropha Curcas L," *Bioresourc Technology*, vol. 67, pp. 73-82, 1999.
- [3] B. K. Barnwal, "Sharma Prospects of biodiesel production from vegetable oils in India," *Renewable and Sustainable Energy Reviews*, vol. 9, pp. 363-378, 2005.
- [4] N. C. O. Tapanes *et al.*, "Transestrification of Jatropha curcas oil glycerides: Thearetical and experimental studies of biodiesel reaction," *Fuel*, vol. 87, pp. 2286-2295, 2008.
- [5] Connemann *et al.*, "Process for the continuous production of lower alkyl esters of higher fatty acids," U.S. Patent, Qct. 11, vol. 5, pp. 354-878, 1994.
- [6] M. P. Dorado *et al.*, "Optimization of alkali-catalyzed transesterification of brassica garinata oil for biodisel production," *Energy and Fuels*, vol. 18, pp. 77-83, 2004.

- [7] T. Pramanik and S. Tripathi, *Biodiesel: Clean fuel of the future hydrocarbon processing*, February 2005, pp. 49-54.
- [8] A. Bouaid *et al.*, "Pilot plant studies of biodisel production using Brassica carinata as row material," *Catalysis Today*, vol. 106, pp. 193-196, 2005.
- [9] A. K. Tiwari et al., "Biodiesel production from Jatropha oil with high free fatty acid: An optimized process," *Biomass and Bioenergy*, vol. 31, pp. 569-575, 2007.
- [10] A. K. Singh *et al.*, "Base-catalyzed fast transesterification of soybean oil using ultrasonication," *Energy and Fuels*, vol. 21, pp. 1161-1164, 2007.
- [11] G. Franceschini and S. Macchietto, "Validation of model for biodiesel production through model- based experiment design," *Ind. Eng. Res*, vol. 46, pp. 220-232, 2007
- [12] W. M. J. Achten *et al.*, "Jatropha bio-diesel production and use," *Biomass and Bioenergy*, vol. 32, pp. 1063-1084, 2008.
- [13] S. K. Saldar *et al.*, "Studies on the comparison of performance and emission characteristics of diesel engine using three degummed nonedible vegetable oils," *Biomass and Bioenergy*, in press.
- [14] S. Stiefel and G. Dassori, "Simulation of biodiesel production through transesterification of vegetable oils," *Ind. Eng. Chem. Res.*, vol. 48, pp. 1068-1071, 2009.
- [15] H. J. Kim *et al.*, "Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst," *Catalysis Today*, vol. 93, pp. 315-320, 2004.
- [16] S. Furuta *et al.*, "Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure," *Catalysis Communications*, vol. 5, pp. 721-723, 2004.
- [17] E. Loters et al., "Synthesis of biodiesel via acid catalysis," Ind. Eng. Chem. Res., vol. 44, no. 14, pp. 5353-5363, 2005.
- [18] V. V. Bokade and G. D. Yadav, "Transesterification of edible on nonedible vegetable oils with alcohols over hetero-polyacids supported on acid-treated clay," *Ind. Eng. Chem. Res.*, vol. 48, pp. 9408-9415, 2009.
- [19] M. Jos é et al., "Preparation and properties of biodiesesl from cynara cardunculus L. oil," *Ind. Eng. Chem. Res.*, vol. 38, no. 8, pp. 2927-2931, 1999.
- [20] H. Fukuda *et al.*, "Biodiesel fuel production by transesterifcation of oils," *Journal of Bioscience and Bioengineering*, vol. 92, no. 5, pp. 405-416, 2001.
- [21] D. Thomas *et al.*, "Effect of biodiesel, biodiesel blends, and a synthetic diesel on emissions from light heavy-duty diesel vehicles," *Environmental Science Technology*, vol. 34, no. 3, pp. 349-355, 2000
- [22] M. Janet *et al.*, "Lubricity- enhancing properties of soy oil when used as blending stock for middle distillate fuels," *Ind. Eng. Chem. Res.*, vol. 41, no. 5, 2002.

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