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Biodiesel Production From Jatropha Oil And Castor Oil By Transesterification Reaction - Experimental And Kinetic Studies

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Abstract: Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gases, with the exception of hydroelectricity and nuclear energy, of all, these sources are finite and at current usage rates will be consumed shortly. From the point of view of protecting global environment and concerns for long term energy security, it becomes necessary to develop alternative fuels with properties comparable to petroleum based fuels. Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods, operation of diesel tractor and pump sets in agricultural sector. Unlike rest of world, India's demand for diesel fuels is roughly six times that of gasoline hence seeking alternative to mineral diesel is a natural choice. Esters from vegetable oils are the best substitutes from diesel because they do not demand any modification in the diesel engine and have a high energetic yield. In the present investigation the potential of Jatropha oil and Castor oil were tested for production of Bio diesel. The properties of the bio diesel synthesized from these two sources were compared with those of the conventional diesel. The kinetic studies of the transesterification reaction to produce bio diesel reveal that the reaction is first order and reversible. The forward and reverse rate constants were evaluated. The temperature dependence of the reactions was modelled using Arrhenius equation and the Arrhenius parameters (Frequency factor K_0 and Activation energy A) are evaluated. The equations for forward and reverse reactions are
Castor oil are $k_1 = k_{01}e^{-A/T} = 0.027e^{-140/T}$;$k2 = k_{02}e^{-A_2/T} = 0.0302e^{-90.91/T}$
Jatrophaoil are $k_1 = k_{01}e^{-A/T} = 0.0608e^{-50/T} k_2 = k_{02}e^{-A_2/T} = 0.0273e^{-75/T}$
Keywords: Biodiesel, Jatropha, Castrol, Kinetics.

Introduction

As petroleum supplies diminish in the world, India becomes increasingly dependent upon foreign sources of crude oil. India currently imports more than 75% of its petroleum and more than 60% of this petroleum is used for transportation fuels. The rising demand in many rapidly developing countries around the world is beginning to create intense competition for the world`s dwindling petroleum reserves. Furthermore, the combustion of petroleum based fuels has created serious concern over global warming effect due to greenhouse gas (GHG) emissions. In response to these global energy concerns and in effort to move the country towards greater energy independence and security, the country has made plans to promote the use of renewable fuels,energy efficiency, and new energy technology research and development[1]. When Rudolph Diesel first demonstrated his compression ignition engine in 1898 World Exhibition at Paris he used peanut oil as the fuel. Diesel engines initially ran on vegetable oils till 1920 when engines were first altered to use petroleum products[8]. Triglycerides are the main constituents of vegetable oils and animal fats[2]. A triglyceride, also called triacylglycerol (TAG), is a chemical compound formed from one molecule of glycerol and three fatty acids. From a chemical point of view, oils from different sources have different fatty acid compositions.

Bio Diesel From Jetropha

Non-edible oils extracted from tree seeds are considered an important source of energy for the future. Among the species producing oilseeds, Jatropha (Jatropha curcas) is the frontrunner as a species for commercial cultivation because of its several advantages over others in this category[3]. In the wake of the interest being generated about Jatropha, a large number of people have entered the scene as stakeholders. Unfortunately, not many of them are well informed about its actual potential as an oilseed bearer for biodiesel production.

The current situation is one where overenthusiastic or unscrupulous promoters are misleading a majority of the prospective Jatropha producers. Tall claims are being made of varieties and vegetative planting material that start producing seed in the first year itself, and have the potential to eventually yield 10 tons of Jatropha seed per ha annually. In reality, however, there does not appear to be a single plantation in India that can substantiate such claims.

BAIF Development Research Foundation in Pune has been conducting research on the cultivation aspects of Jatropha for the past six years on its farm in Tiptur in Karnataka. It also organised a National Workshop on the subject in 2003. Since then, BAIF has been serving as an information network centre for those interested in tree-borne oilseed species (4). The current paper combines the research experience with information gathered through interaction and from literature on oilseeds for biodiesel production.

Advantages Of Jatropha

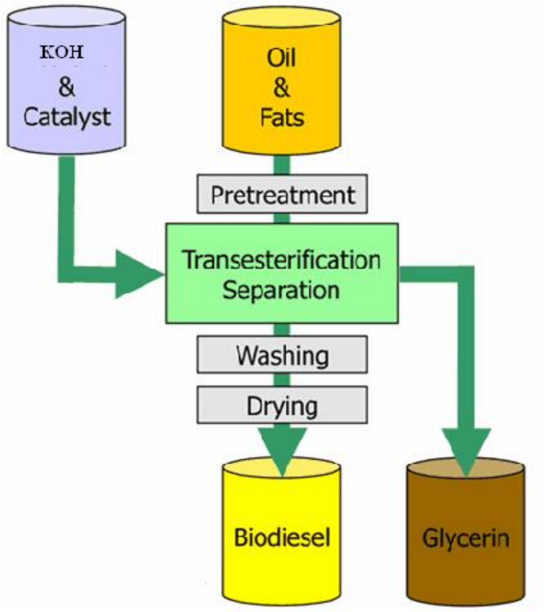
Apart from Jatropha, the category of tree-borne oilseed species includes Karanj (Pongamia pinnata), Mahua (Madhuca latifolia and M. indica), Undi (Calophyllum inophyllum), Neem (Azadirachta indica) and Simarouba (Simarouba glauca). Jatropha has an advantage over others in many ways[5]. It is at a higher stage of domestication than others and hence considerable research has been carried out already to understand the species and its cultivation.

Unlike most other perennial species, Jatropha has a shorter gestation period and regular seed harvests are possible within four years of establishment. Being a small tree with a lax canopy, it is ideally suited for small farm agroforestry systems. Its natural distribution throughout India is indicative of its adaptation to diverse agro-climatic conditions[6]. Moreover, farmers are familiar with Jatropha as a hardy fence plant that can survive with very little inputs or management. These advantages notwithstanding, it should not be assumed that Jatropha can succeed under any condition.

Another advantage of Jatropha is the properties of its oil for biodiesel production. Its very low Free Fatty Acid content, almost similar to edible oils, makes it ideal for transesterification and the oil to biodiesel conversion ratio is higher than in other non-edible oils. A higher ratio means better profit margins and hence Jatropha oil is a more desirable raw material than the oils of other tree seeds[7]. Combustion studies have also shown Jatropha biodiesel to be superior to others as its emissions are less polluting than that of others.

Transesterification

Transesterification can be carried out by either acid catalyst or alkali catalyst. The term transesterificationrefers to ester interchange reaction is conversion of one ester to other. This includes all combinations of interaction between monohydroxy alcohol esters, mono and diesters of glycol mono di and triglycerides and the various esters of tetrahydroxy and higher alcohol are possible[8]. The ester – ester interchanges of materials intended for non edible industrial uses are undoubtedly becoming increasingly important when applied to fats and oils ester – ester interchange may improve physical properties because it changes the acyl group arrangement within the components of the mixed triglycerides of fats and oils ester – ester interchange may be effected without catalyst at high temperature 150^0 C and above.Ester- ester interchange occurs at rapid rate and at less temperature by use of either acid or alkaline catalyst[9]. Ester interchanges proceed at random.This will result in compositional changes, the fatty acyl groups within triglyceride to all the possible combination.



Benefits Of Transesterification

Transesterification is widely used to reduce vegetable oil viscosity. Most industrial processes employ alkaline catalysis and methanol. In almost all countries methanol is more available than ethanol. The transesterification process reduces the molecular weight to ca. 1/3 in relation to the triglycerides, and also, reduces the viscosity and improves the volatility.

Kinetics

Freedman etal performed trails with peanut, soy, and sunflower oils at 60^0 C using methanol and sodium methaxide as a catalyst and found that around 80% of the conversion of esters occurs within the first few minutes of the reaction and after an hour it reaches a range of about 93-97%. When an acid catalysts is used reaction time can be much longer. The temperature of the transesterification, its catalysts and quantity , the alcohol and its moral relation with the tyiglycerides depends on the oil or the fat that is being used. between methanol and vegetable oil is 3.3 to 5.5:1 acid show higher cetane number, higher cloud point and cause nozzel clogging. Esters prepared with very unsaturated fatty acid show low cetane number and suffer oxidation easily[10]. Generally, cetane number, heat of combustion, melting point and viscosityof neat fatty compounds increase with increasing with increasing chain length and decrease with increasing unsaturation.

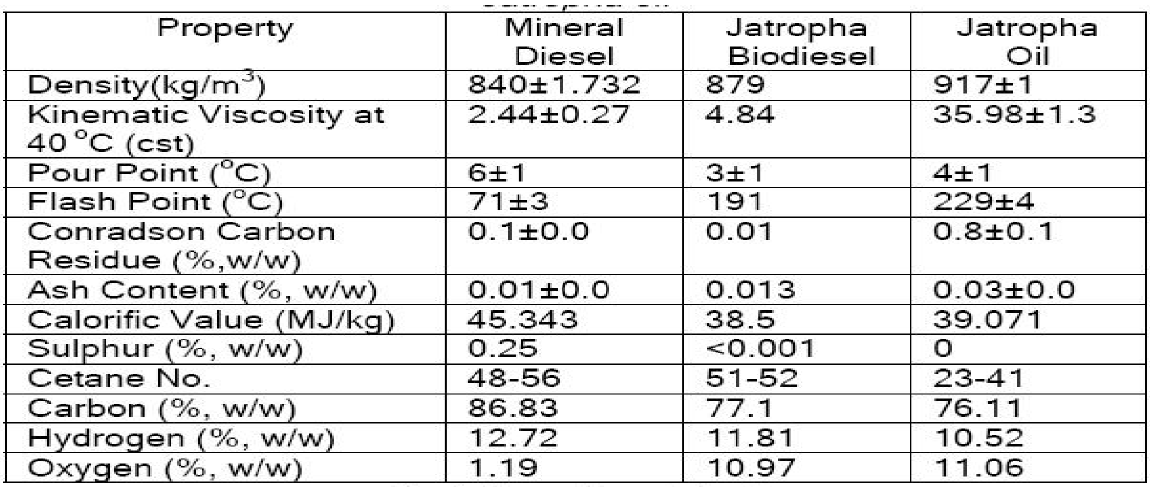
Experimental

Initially the oil was heated to remove the moisture associated with it and about 250 ml of oil was heated at a temperature of 50^oC in constant temperature bath. 2.5 g of potassium hydroxide (KOH) was dissolved in about 50 ml of n-butanol (Potassium Butoxide), it was agitated for a few minutes till the catalysts gets completely dissolved in butanol then it was heated in a constant temperature bath at 50^o C for a few minutes after the temperature attains steady state.The oil and potassium butoxide (KOH+ n – butanol) that was heated separately at 50 ^{o} C was taken out, then transferred the potassium butoxide to oil, the contents were mixed thoroughly.About 60ml of this mixture was exactly measured and transferred to each of the four round bottomed flasks fitted with condenser, the set was placed in a water bath.Heating is continued initially at a temperature of 50^oC in a constant temperature bath. After an interval of 30 minutes the first flask was drawn from the temperature bath assembly and kept in ice mixture to arrest the reaction to further proceed.The second, third and fourth flask were drawn at a time interval of 45,60 and 75 minutes respectively. The mixture was then poured into separating funnel and shaking it, allowed to stand for some period of time. The mixture will soon form two layers: one is glycerol which is the bottom layer and the top layer is comprised of butyl ester. The two phases glycerol phase and butyl ester phase were noted individually.

The two layers were individually collected in an amber bottle. The procedure was repeated as above for various temperatures. Finally the properties for the glycerol can be determined in a gas chromotography (GC). Experiments were repeated for 4 different temperatures, 50°C, 60°C, 70°C and 80°C respectively. The percentage conversion for transesterification reaction was calculated for each run. From the percentage conversion vs time data for each temperature the kinetic data such as order of reaction and the rate constant will be estimated. The effect of temperature on the rate constant will also be estimated and the Arrhenius frequency factor and the activation energy for reaction are estimated.

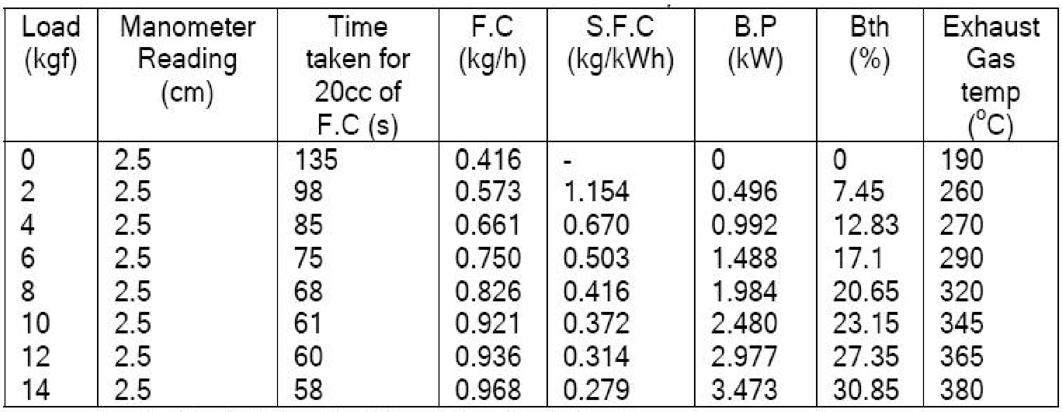
Oil + Butanol ↔ Glycerol + Butylester(Transester)

Properties Of Diesel Fuel And Biodiesel



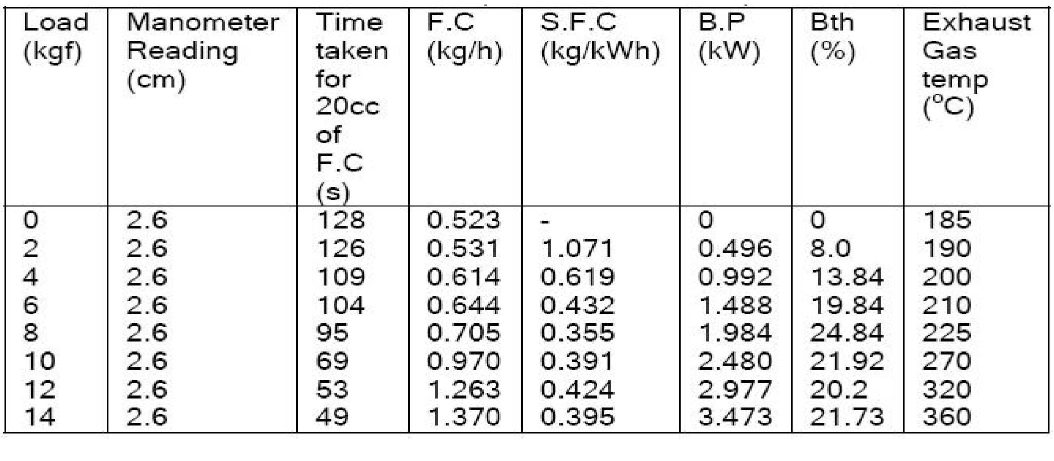
Property	Mineral Diesel	Jatropha Biodiesel	Jatropha Oil
Density(kg/m^3)	840±1.732	879	917±1
Kinematic Viscosity at 40 °C (cst)	2.44±0.27	4.84	35.98±1.3
Pour Point (°C)	6±1	3±1	4±1
Flash Point (°C)	71±3	191	229±4
Conradson Carbon Residue (%,w/w)	0.1±0.0	0.01	0.8±0.1
Ash Content (%, w/w)	0.01±0.0	0.013	0.03±0.0
Calorific Value (MJ/kg)	45.343	38.5	39.071
Sulphur (%, w/w)	0.25	<0.001	0
Cetane No.	48-56	51-52	23-41
Carbon (%, w/w)	86.83	77.1	76.11
Hydrogen (%, w/w)	12.72	11.81	10.52
Oxygen (%, w/w)	1.19	10.97	11.06

Combustion properties of diesel



Load (kgf)	Manometer Reading (cm)	Time taken for 20cc of F.C (s)	F.C (kg/h)	S.F.C (kg/kWh)	B.P (kW)	Bth (%)	Exhaust Gas temp (°C)
0	2.5	135	0.416	-	0	0	190
2	2.5	98	0.573	1.154	0.496	7.45	260
4	2.5	85	0.661	0.670	0.992	12.83	270
6	2.5	75	0.750	0.503	1.488	17.1	290
8	2.5	68	0.826	0.416	1.984	20.65	320
10	2.5	61	0.921	0.372	2.480	23.15	345
12	2.5	60	0.936	0.314	2.977	27.35	365
14	2.5	58	0.968	0.279	3.473	30.85	380

Combustion properties of biodiesel



Load (kgf)	Manometer Reading (cm)	Time taken for 20cc of F.C (s)	F.C (kg/h)	S.F.C (kg/kWh)	B.P (kW)	Bth (%)	Exhaust Gas temp (°C)
0	2.6	128	0.523	-	0	0	185
2	2.6	126	0.531	1.071	0.496	8.0	190
4	2.6	109	0.614	0.619	0.992	13.84	200
6	2.6	104	0.644	0.432	1.488	19.84	210
8	2.6	95	0.705	0.355	1.984	24.84	225
10	2.6	69	0.970	0.391	2.480	21.92	270
12	2.6	53	1.263	0.424	2.977	20.2	320
14	2.6	49	1.370	0.395	3.473	21.73	360

Results And Discussions

Kinetic Studies

The transesterification reaction is of the form A +B = C + D.

In order to determine the rate constants it was initially assured that the reaction is irreversible and the order is 2. Integral method was used to verify the kinetics for the second order irreversible reaction. A plot of $X_A/(1 - X_A)$ vs 't' should give a straight line passing through the origin and its store is CA_o since $X_A/(1 - X_A) = KCA_o t$.Conversion for each reading was calculated as indicated in table 5. The calculated results for all the readings are shown in the table 6. A plot of $X_A/(1 - X_A)$ vs t does not give a straight line(refer fig. 1) indicating that the nature and the order are not right, hebce it was decided to fit the data for first order reversible reaction. For such a scheme the rate equation in the integrated form is $-\ln[(1 - X_A)/X_A] = k_1 t/X_{Ae}$.Hence a plot of $-\ln[(1 - X_A)/X_{Ae}]$ vs t will yield a straight line passing through the origin and having a slope k_1/X_{Ae}.The results indicate that the transesterification is a reversible reaction of first order. It holds good for both castor oil and jatropha oil. The consolidted value of k1 and k2 are given in table .

For castor oil,the effect of temperature on rate constant is assumed to be similar to that of Arrhenius equations.

$$\mathbf{k1 = k_{01}e^{-A1/T}\ (forward\ reaction)}$$

$$\mathbf{k2 = k_{02}e^{-A2/T}\ (backward\ reaction)}$$

For Jatropha Oil Final Values

Tempreture(k)	K	K1	K2	1|T	1n K1	1nK2
303	2.023	0.0525	0.0262	0.0033	-2.946	-3.642
313	3.127	0.0679	0.0215	0.00319	-2.689	-3.839
323	9.845	0.0809	0.008	0.00395	-2.514	-4.828
333	11.125	0.0895	0.0081	0.003	-2.414	-4.816

The analysis reveals that the kinetics of transesterificationcan be represented by the following equations:

For Castor Oil: $\mathbf{dX_A/dt = k_1(1 - X_A) - k_2X_A;\ k_{01}e^{-A1/T}(1 - X_A) - k_{02}e^{-A2/T}X_A}$

For Jatropha Oil: $\mathbf{dX_A/dt = k_1(1 - X_A) - k_2X_A\ ;\ k_{01}e^{-A1/T}(1 - X_A) - k_{02}e^{-A2/T}X_A}$

For Castrol Oil Final Values

Temperature (K)	K	K1	K2	1|T	1n k1	1nK2
303	0.5882	0.0233	0.0419	0.0033	-3.759	-3.171
313	1.206	0.2419	0.2175	0.00319	-1.419	-1.525
323	1.4599	0.0301	0.0206	0.00309	-3.503	-3.882
333	2.983	0.0325	0.0125	0.003	-3.426	-4.382

Conclusion

The experiments indicate that Jatropha gives higher biodiesel yieldthan Castor oil.Transesterification reaction is first order reversible reaction because oil was taken in excess compared to methanol.The kinetic equations are

1. Castor Oil
   $k_1 = k_{01}e^{-A/T} = 0.027e^{-140/T}$
   $k2 = k_{02}e^{-A_2/T} = 0.0302e^{-90.91/T}$
2. Jatropha Oil
   $k_1 = k_{01}e^{-A/T} = 0.0608e^{-50/T}$
   $k_2 = k_{02}e^{-A_2/T} = 0.0273e^{-75/T}$.

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