

Transesterification, Modeling and Simulation of Batch Kinetics of Non-Edible Vegetable Oils for Biodiesel Production

Pankaj Tiwari, Rajeev Kumar and Sanjeev Garg
Department of Chemical Engineering, IIT Kanpur, 208 016, India

Abstract

Biodiesel derived from renewable plant sources is monoalkyl esters of long chain fatty acids which fall in the carbon range C_{12} - C_{22} . It has similar properties as mineral diesel. Various processes exist to convert vegetable oils (mainly triglycerides) into biodiesel. Transesterification of vegetable oils using alcohol in a catalytic environment is most commonly used method for producing biodiesel. The equilibrium conversions of Triglycerides (TG) is affected by various factors, namely, type of alcohol used, molar ratio of alcohol to TG, type of catalyst, amount of catalyst, reaction temperature, reaction time and feedstock quality (like free fatty acid content, water content etc.).

The present work reports the characterization of non-edible feedstock oils of Indian origin, production, separation, characterization of biodiesel and byproduct. This study also reports the optimal operating parameters for different oils in batch reactor. The main thrust of the present work was to study the kinetics, modeling and simulation of alkali-catalyzed transesterification of Linseed and *Jatropha curcas* oils. Experiments were carried out in a 2.0 l batch reactor to generate kinetic data and a reversible kinetic model was developed. The effects of temperature, catalyst concentrations, and molar ratios of methanol to TGs and stirring rates were investigated. A few fuel properties were also measured for biodiesel to observe its competitiveness with conventional diesel fuel.

The equilibrium conversions of TG were observed to be in the range of 88-96 %. (Linseed) and 50-83% (Jatropha). The equilibrium conversions were achieved in less than 45 minutes for both oils. It was also observed that increasing the temperature and molar ratio increased the equilibrium conversions; while increase in catalyst concentration had no significant effect on reaction time. Characterization of the feedstock oils and biodiesel produced were carried out. It was observed that the biodiesel produced had similar properties to mineral diesel.

Model parameters (order and rate constants) for the reversible model were calculated. Gear's technique was used to solve the initial value problem and genetic algorithm was used with the mathematical model to minimize the error between experimental and model predicted conversions. Activation energies for forward and backward reactions were estimated. Model fitness values were observed to be more than 0.9. Various simulations were also carried out at different conditions and showed that beyond a critical molar ratio there is no significant effect on transesterification kinetics.

Introduction

Presently the world's energy needs are met through non-renewable resources such as, petrochemicals, natural gas and coal. These resources will be depleted in few years as a result of continued increase in the demand and the cost of petroleum based fuels and the present pattern of consumption. Petroleum fuels also deteriorate the ambiance and cause global warming. In diesel engine emissions, using mineral diesel, the presence of sulphur results in

sulphur oxides and sulfates.¹⁻² When these sulfur chemicals are released into the atmosphere they form sulfur dioxide which combines with water to form sulfuric acid. This acid is carried by winds to neighboring regions, dropping onto the land and its inhabitants when it rains, or is misty, or foggy. This phenomenon is known as acid rain.

Substitution of a small fraction of the total diesel fuel consumption by alternative fuels will have a significant impact on economy and the environment. Hence efforts are being made to explore for alternative sources of energy that are technically feasible, economically competitive, and environmentally acceptable and readily available.³⁻⁴ Biodiesel is one of such promising alternative fuels. It is derived from vegetable oils (edible or non-edible) and animal fats. Straight vegetable oils can also be used as fuel in diesel engine, but direct use of vegetable oils poses many problems in the long run, namely, injector chocking, ring sticking, wax formation, carbon deposits, misfire, ignition delay and in fuel atomization.⁵⁻⁹ These problems are attributed to high viscosity, low volatility, polyunsaturation, high flash point and low cetane number. These properties can be improved by various physical and chemical means and the associated problems can be counteracted.

Biodiesel is free from sulphur (as it is derived from vegetable oils) and its use substantially reduces the emissions of SO₂ and aromatics as well.^{1, 7-8} Biodiesel does not cause acid rains and its blends also help in reducing the effects of acid rains. The usage of biodiesel, thus, is in amity with the environment. Moreover, it reduces the particulates and many aromatic hydrocarbons,^{1, 7-8} which otherwise cause many diseases. Even on blending with mineral diesel, biodiesel significantly reduces emissions^{1, 9}. Its combustion does not increase net atmospheric levels of greenhouse gases, e.g., CO₂ as it is obtained from plants and not from fossil fuels. Biodiesel results in a balanced carbon cycle in environment. It reduces lifecycle of CO₂ emissions by over 78 % compared to mineral diesel.⁸ It is reported that most of the emissions reduce while using biodiesel with the exception of nitrogen oxides, which either remain the same or are slightly increased.⁸⁻⁹ Moreover, due to certain other properties, like being biodegradable and non-toxic, having high flash point and cetane number, biodiesel is being viewed as a suitable alternative to mineral diesel.

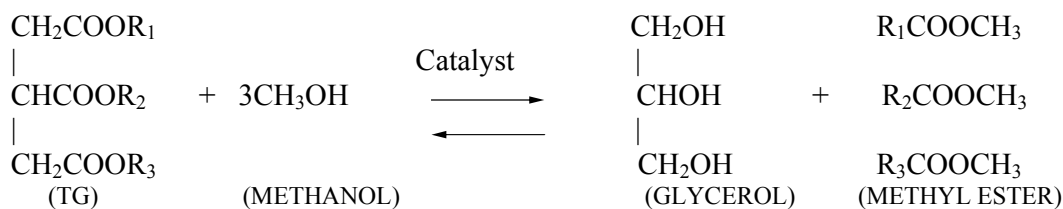
Efforts have already been made to develop vegetable oil derivatives that approximate the properties and performance of mineral diesel. Predominately, four ways are reported in literature to improve the properties of vegetable oils - dilution, thermal cracking, microemulsion, and transesterification.^{5,10} Transesterification process is one of the most successful and promising processes to convert vegetable oils into diesel-like liquid, biodiesel. Chemically, biodiesel is mono-alkyl esters (fatty esters) of long chain fatty acids (falls in carbon range from C₁₂-C₂₀) derived from renewable biological sources such as vegetable oils or animal fats.^{5, 11}

Selection of vegetable oil for biodiesel production is the key factor to reduce the cost of manufacturing. This selection depends on three factors. *Firstly*, the nature and availability of the vegetable oil is important. For example, soybean oil is being used in America, soybean oil and sunflower oil (both are edible oils) are being used in most of the European countries. In developing countries like India, land availability even for food grain is insufficient and edible oils are mostly being used in the food sector. Population of India is projected to be 1.44 billion by the year 2030. To meet the demand, India should achieve a grain production of 267 Mty⁻¹.¹² Without any increase in the area for food crops, projected grain production will be 222 Mt, which will fall short by 45 Mt¹²⁻¹³ Therefore, the existing agricultural land cannot be used for vegetable oil cultivation for biodiesel production. The potential solutions for

producing vegetable oils meant for biodiesel in India are the lands presently used by crops with low production, degraded pastures and forestlands. India has more than 100 Mha of waste and degraded land which can be utilized for production of non-edible oils.¹²⁻¹³ Thus, India and other developing countries do not have sufficient edible to full fill the requirement of food sector, and as a result these are being imported. *Secondly*, the price is very important. Costs of edible oils in developing countries are high because of high import bill. Moreover, non-edible oils availability is region specific and they find usage in other sectors and hence the prices could be very high limiting the economic production of biodiesel. *Thirdly*, the policies and planning to produce non edible vegetable oils on waste and arid land in large excess from government and other non-government organizations are important. These will aid in production of non edible oils.

India and other developing countries can secure the green-energy dream in their own geographical boundaries. Linseed and *Jatropha curcas* are two of such non-edible vegetable oils and viable feedstocks for the production of renewable, biodegradable and nontoxic fuel (biodiesel). *Jatropha curcas* is being adopted as a major feedstock oil option to produce biodiesel world wide. *Jatropha curcas* (Euphorbiaceae) is a genus comprising 70 species distributed in tropical and sub-tropical parts of the world, of which nine species occur in India.¹⁴ *Jatropha curcas* is commonly known as physic nut, Ratanjyot, Chandrajyoti, Chandraprabha, Wild castor or Nepalm. *Jatropha* plant thrives on any type of soil (semiarid and arid with minimal care), can survive a long period of drought and the meal left after extraction of the oil is an excellent manure.

Batch Transesterification reaction



Transesterification process is a set of three consecutive chemical reactions between ester (TGs present in vegetable oils) and an alcohol in presence of a catalyst (homogeneous or heterogeneous). Alkyl esters in the carbon range C₁₂-C₂₀ result and are known as ‘biodiesel’ with glycerol as a byproduct. Transesterification reaction is sensitive to reaction parameters like, alcohol used, molar ratio of alcohol to oil (MR), temperature of the reaction (T), catalyst and catalyst amount (C % w/w of oil), and stirring rate (SR). The schematic of the overall transesterification reaction as shown above requires three moles of methanol to react with one mole of TGs. This overall reaction is reversible. To shift the equilibrium conversion in the forward direction (to get more yield of ME) either the molar ratio (methanol to oil) of the reaction should be increased or one of the products of the reaction should be separated and removed continuously.

The process developed by Freedman et al.¹⁵ for alkali catalyzed transesterification is widely referred for experimental details and protocols for batch scale setups. A two litre glass reactor was equipped with an anchor-shaped glass stirrer, a K type thermocouple, a water condenser and funnel, and was surrounded by a heating mantle controlled by a proportional integral

derivative (PID) temperature controller device. Molar ratio of 6:1 was used; temperature was kept at 60°C, stirring at 600 rpm and 1% (w/w) of sodium methoxide catalyst was used. Samples of 10 ml (approximately 8 gm) were drawn from the reaction mixture at regular intervals, typically 10 min, neutralized and analyzed by gas chromatography (GC). Wimmer¹⁶ reported blending 27.6 gm of KOH, 240 ml of methanol and 1618 gm of unrefined rape oil and stirring for 20 min. This process was one of the first using unrefined oil. Approximately 3.0 h were required for the completion of the reaction. Finally, 80 ml of water was added and mixture was allowed to settle overnight at room temperature. The glycerol was separated from the esters due to density difference. These fatty acid esters were used without further purification. Ramadhas et al.¹⁷ reported the use of acid catalyst followed by alkali catalyst in a single process using rubber seed oil with high FFA content. The objective of their study was to develop a process for producing biodiesel from low-cost feedstock oils like crude rubber seed oil. The first step of the integrated process reduces FFA content to less than 2%. One litre of crude rubber seed oil was reacted with 200 ml of methanol for the acid esterification process. The temperature, catalyst, pressure, and time of the reaction were 50°C, 0.5% (w/w) H₂SO₄, 1 atmosphere, 20-30 min respectively. On completion of reaction, the excess alcohol and impurities were separated out from the top layer. The lower layer was separated for second step. Subsequently, it was transesterified to monoesters of fatty acids using alkaline catalyst. NaOH (5 gm) was used as alkali catalyst, temperature was kept at 45 ± 5°C, and reaction was carried out for 30 min. After completion of reaction the products were allowed to separate in two layers. The lower layer consisting of impurities and glycerol was drawn off. The esters remained in the upper layer. Methyl esters were washed to remove the entrained impurities and glycerol. Hot distilled water (10% by volume) was sprayed over the surface of esters and stirred gently. Lower layer was discarded and yellow color layer (biodiesel) was separated.

Variables affecting transesterification reaction

The transesterification process is affected by various operating factors used. The effects of these factors as reported in literature are described below.

Effect of free fatty acid and moisture content

The free fatty acid (FFA) and moisture content are the key parameters for determining the viability of vegetable oils to be used in transesterification process. Most of the biodiesel is currently made from edible oils by using methanol and alkali catalysts.¹⁸⁻²¹ To carry out this reaction to completion, less than 3% FFA content in oils is needed.³ Higher the acidity of the oil, smaller is the conversion efficiency. Excess as well as insufficient amount of catalyst may cause soap formation.²¹ However, there are large amounts of low cost oils (fried and waste oil) and fats that could be converted to biodiesel. The problems with processing these low cost oils and fats are that they often contain large amounts of free fatty acids that cannot be converted to biodiesel using alkali catalyst.¹⁰ Therefore, a two-step esterification process is required for these feedstocks.²²⁻²³ Initially, the FFA of these oils can be converted to fatty acid methyl esters (FAME) by an acid catalyzed pretreatment and the second step transesterification is completed by using alkali catalyst. Zullaikah et al.²³ have successfully made biodiesel from Rice-bran oil with high FFA content. A two-step acid-catalyzed methanolysis process was employed for the efficient conversion of Rice-bran oil into FAME (or biodiesel). The first step was carried out at 60°C. Depending upon the initial FFA content of oil, 55-90% FAME content in the reaction product was obtained. More than 98 % FFA and less than 35% conversion of TG were observed in 2 hr. The organic phase of the reaction product from first step was used as the substrate for an acid-catalyzed methanolysis at 100°C in the second step. By this method, more than 98% FAME was obtained in less than 8h. The

method can be used for feedstock stored for long time or feedstock containing high FFA content. Ma et al.²⁴ studied the transesterification of beef tallow catalyzed by NaOH in presence of FFAs and water. Without adding FFA and water, the apparent yield of beef tallow methyl esters (BTME) was highest. When 0.6% of FFA was added, the apparent yield of BTME reached the lowest, less than 5%, with any level of water added. Turck et al.²⁵ have investigated the negative influence of base catalyzed transesterification of TGs containing substantial amount of FFA. FFAs react with the basic catalyst added for the reaction and give rise to soap, as a result of which, one part of the catalyst is neutralized and is therefore no longer available for transesterification.

Molar ratio of alcohol to oil and type of alcohol

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to TG. Stoichiometrically, three moles of alcohol and one mole of TG are required for transesterification to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium controlled reaction in which excess of alcohol is required to drive the reaction in the forward direction.³ For achieving maximum conversions, a molar ratio of 6:1 is recommended for alkali catalyzed transesterification reactions.^{3, 26} The molar ratio has no effect on acid, peroxide, saponification and iodine values of methyl esters.²⁷ The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while an alkali catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time studied by Freedman et al.²⁶, Bradshaw and Meuly²⁸ stated that the practical range of molar ratio was 3.3-5.25:1::methanol:vegetable oil. The ratio of 4.8:1 was used in some examples, with reported yield of 97- 98%, depending upon the quality of the oils. For a three step transesterification process used, the ratio was reduced to 3.3:1. Methanol present in amounts of above 1.75 equivalents posed problems in the gravity separation of the glycerol, thus adding more cost to the process. Higher molar ratios resulted in greater ester conversions in a shorter time. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerol than did a 3:1 molar ratio.²⁰ Rapeseed oil was methanolized using 1% NaOH or KOH and it was observed that a molar ratio of 6:1 (methanol to oil) gave the best conversion. When large amount of free fatty acids were present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis.²⁹ Freedman et al.³⁰ studied the effect of molar ratio (from 1:1 to 6:1, methanol to oil) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversions (93-98%) at a 6:1 molar ratio. Tanaka et al.³¹ in their novel two-step transesterification of oils and fats such as coconut oil, palm oil and tallow used 6:1-30:1 molar ratios with alkali catalyst to achieve a conversion of 99.5%. A molar ratio of 6:1 was used for beef tallow transesterification with methanol by Ali and Zhang.³² They reported that 80% (by tallow weight) esters were recovered in their study.

Effect of catalyst and catalyst amount

Catalysts used for the transesterification of TGs are alkalies, acids, enzymes or heterogeneous catalysts. Among these alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, and potassium methoxide are more effective.¹⁰ If the oil has high FFA content and more water, acid catalyzed transesterification is suitable.³³ The acids being used are sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid.³⁰ Methanolysis of beef tallow was studied with catalysts NaOH and NaOMe. Comparing the two catalysts, NaOH was significantly better than NaOMe. The catalysts NaOH and NaOMe reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow, respectively.^{24, 34} Sodium methoxide causes formation of several byproducts mainly sodium salts, which are to be

treated as waste. In addition, high quality oil is required with this catalyst.^{3, 36} This was different from previous reports in which ester conversion at 6:1 molar ratio of alcohol to oil for 1% NaOH and 0.5% NaOMe were almost the same after 60 min.²⁷ Some of the difference were attributed to the differences in the reaction system used.³ In alkali catalyzed methanolysis, mostly sodium hydroxide or potassium hydroxide have been used in concentration from 0.4 to 2% w/w of oil.³⁵ Refined and crude oils with 1% either sodium hydroxide or potassium hydroxide catalyst resulted in successful conversion. Methanolysis of soybean oil with 1% potassium hydroxide gave the best yields and viscosities of esters.^{26, 36} Attempts have been made to use basic alkaline-earth metal compounds in the transesterification of rapeseed oil for production of FAMES. The reaction proceeds if methoxide ions are present in the reaction medium.³⁶⁻³⁹ The alkaline-earth metal hydroxides, alkoxides and oxides catalyzed reaction proceeds slowly as the reaction mixture constitutes a three-phase system: oil-methanol-catalyst, which for diffusion reasons inhibits the reaction. The catalytic activities of magnesium oxide, calcium hydroxide, calcium oxide, calcium methoxide, barium hydroxide, and for comparison, sodium hydroxide during the transesterification of rapeseed oil were investigated. Sodium hydroxide exhibited the highest catalytic activity in this process. The degree to which the substrates were reacted reached 85% after 30 min of the process and 95% after 1.5 h, which represented a close value to the equilibrium. Barium hydroxide was slightly less active with a conversion of 75% after 30 min. Calcium methoxide was medially active. The substrates were reacted to 55% after 30 min, 80% after 1 h and the reaction reached equilibrium (93%) after 2.5 h. The rate of reaction was slowest when catalyzed by calcium oxide. Magnesium oxide and calcium hydroxide showed no catalytic activity in rapeseed oil methanolysis.³⁶ Acid catalyzed transesterification was studied with waste vegetable oil by Mohamad et al.⁴⁰ The reaction was conducted at four different catalyst concentrations, 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the results were compared with 2.25 M H₂SO₄. A decrease in viscosity was observed with HCl though H₂SO₄ had superior catalytic activity in the range of 1.5–2.25 M concentration. Although transesterification with an alkali catalyst gives high conversions of TGs to their corresponding methyl esters in short reaction times, the reaction has several drawbacks. It is energy intensive. Recovery of glycerol is difficult. The acid or alkali catalyst has to be removed from the product. Alkaline waste water requires treatment. FFAs and water interfere with the reaction.³ Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of TGs in either aqueous or non-aqueous systems, which can overcome the problems mentioned above.⁴¹⁻⁴⁶ The time to reach equilibrium conversion is much more than that for alkali or acid catalyzed reactions.^{3,46} In particular, the byproduct, glycerol can be easily removed without any complex process, in enzyme catalyzed reactions, and the free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, the production cost of a lipase catalyst is significantly greater than that of an alkali catalyst. Lipase catalyzed reactions have the advantage of reacting at room temperature without producing spent catalysts. The commonly used enzymes in biodiesel production are *Candida antarctica*, *Novozym 435*, *Candida rugosa*, *Pseudomonas cepacia*, *Pseudomonas fluorescens*, *Candida cylindracea*, *Mucor miehi*, *R. oryzae IFO*, *IM BS-30*. The enzymes can be recycled for use again or immobilized onto a substrate. If immobilized, the substrate will require replacement when yields begin to decline. The enzyme reactions are highly specific. The excess alcohol is reported to be inhibitory to some enzymes and hence a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 mole ratio each. Generally, these reactions are very slow, with a three step sequence requiring from 4 to 40 h, or more. The reaction conditions are also modest, from 35 to 45°C.⁴⁶ Iso et al.⁴⁵ studied the transesterification using immobilized lipase in non-aqueous conditions. Immobilized *Pseudomonas fluorescens* lipase showed the highest

activity in this reaction. The activity of immobilized lipase was highly increased in comparison with free lipase because its active sites became more effective. The main advantage of enzyme as a catalyst was to increase the yield of biodiesel in presence of water in the feedstock. Nouredini et al.⁴⁶ have investigated the biodiesel production using lipase catalyst. The time taken to achieve 67% yield of biodiesel was 72h at room temperature. However, the energy input was zero. Moreover, the time to reach equilibrium conversion was much more than that for alkali or acid catalyzed reactions.⁴⁵⁻⁴⁶

Effect of reaction time and temperature

The rate of reaction is strongly influenced by reaction temperature. However, the reaction proceeds to near completion even at room temperature in sufficient time.^{3,10} Smith⁴⁷ studied methanolysis of castor oil to methyl ricinoleate. The reaction proceeded most satisfactorily at 20-35°C with a molar ratio of 6:1-12:1 and 0.005-0.35% (by weight of oil) of NaOH catalyst. Generally, the reactions were conducted close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. These mild reaction conditions, however, required the removal of FFAs from the oil by refining or pre-esterification. The pretreatment was not required if the reaction was carried out under high pressure (9000 kPa) and high temperature (240°C). Under these conditions, simultaneous esterification and transesterification took place.⁴⁸ This is known as *Super Critical Alcoholysis Process* and there was no catalyst used in the reaction. Freedman et al.³⁰ transesterified peanut, cotton-seed, sunflower and soybean oil under the conditions of methanol-oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1h, the conversion was almost the same for all four oils (93-98%). Ma et al.²⁴ studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to mixing and dispersion of methanol into beef tallow. From 1 to 5 min, the reaction proceeded very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min. Transesterification was carried out at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied at three different temperatures. After 0.1h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1h, ester formation was identical for 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters.¹⁰ The maximum yield of esters occurs at temperatures ranging from 60 to 80°C at a molar ratio (alcohol to oil) of 6:1.⁵⁰ Further increase in temperature is reported to have a negative effect on the conversion.⁵ The butanolysis and methanolysis of soybean oil were studied at different temperatures in the presence of acid and alkali catalysts. These studies indicated that given enough time, transesterification proceeded satisfactorily at ambient temperatures in the case of the alkali catalyst.²⁷ Temperature influenced the reaction rate and esters yield.⁵ The conversion approaches to equilibrium conversions with increased reaction times.³

Effect of stirring rate

Mixing by stirring is very important for transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol solution. The reaction can become diffusion-controlled as poor diffusion between the phases results in a slow rate. As methyl esters are formed, they act as a mutual solvent for the reactants and a single-phase system is formed. Once the two phases are mixed and the reaction is started, stirring is no longer needed. The effect of mixing on transesterification of beef tallow was studied by Ma et al.²⁴ No reaction was observed without mixing. When NaOH-MeOH was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was observed to be

the only controlling factor in determining the yield of methyl esters. This suggested that the stirring speeds investigated exceeded the threshold requirement of mixing.

Effect of using organic cosolvents

The methoxide catalyzed methanolysis of soybean oil at 40°C (methanol–oil molar ratio 6:1) to form methyl esters was observed to proceed more slowly than butanolysis at 30°C.²⁷ This was interpreted to be a result of a two phase reaction in which methanolysis occurred only in the methanol phase. Low oil concentration in methanol caused the slow reaction rate; a slow dissolving rate of the oil in methanol caused an initiation period. Intermediate mono- and diglycerides preferentially remained in the methanol, and reacted further, thus explaining the deviation from second order kinetics.

The same explanations were applied for hydroxide ion catalyzed methanolysis. In order to conduct the reaction in a single phase, cosolvents like tetrahydrofuran (THF), 1, 4- dioxane and diethyl ether were tested. Although, there were other cosolvents, initial study was conducted with tetrahydrofuran. The process which used cosolvent and was free from any kind of catalyst use is known as *Biox Process*.⁴⁸

At 6:1 methanol–oil molar ratio, the addition of 1.25 volume of tetrahydrofuran per volume of methanol produced oil dominant one phase system in which methanolysis speeded up dramatically and occurred as fast as butanolysis. In particular, THF was chosen because its boiling point of 67°C, which was only two degrees higher than that of methanol. Therefore, at the end of the reaction the unreacted methanol and THF could be co-distilled and recycled.⁴⁹ Using tetrahydrofuran, transesterification of soybean oil studies have been carried out with methanol at different concentrations of sodium hydroxide. The ester contents in the reaction mixture after 1 min for 1.1, 1.3, 1.4 and 2.0% sodium hydroxide catalyzed reactions were 82.5, 85, 87 and 96.2%, respectively. Results indicated that the hydroxide concentration could be increased up to 1.3 wt%, resulting in 95% methyl ester after 15 min.⁵⁰ Similarly, for transesterification of coconut oil using a volume ratio 0.87 of THF/MeOH with 1% NaOH catalyst, the conversion was 99% in 1 min.⁵¹ An improved process was investigated for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plant and animals. The process comprised solubilizing oil or fat in methanol or ethanol by addition of a cosolvent in order to form a one-phase reaction mixture, and adding an esterification catalyst. The process proceeded quickly, usually in less than 20 min, at ambient temperatures and atmospheric pressure without agitation. The cosolvent increased the rate of reaction by making the oil soluble in methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the process could be used as biofuels and were found suitable as diesel fuel replacements or additives.⁵²

Experimental Methodology

The major constituents of vegetable oils are TGs (90-98%) and the rests are di- and mono-glycerides. The main key factors during transesterification reaction are percentage of the presence of free fatty acid and moisture, because these two favor the side reactions like saponification and hydrolysis and lower the yield of methyl ester. Thus before proceeding transesterification reaction the characterization of feed stock must be performed to take the judgment for transesterification reaction, either one or two steps. If FFAs presence goes beyond the limit, two step process, first neutralization of FFAs with acid (esterification) and then transesterification with alkali catalyst should be applied to get the higher yield of ME. It was observed that percent of FFAs in Linseed and *Jatropha curcas* are 1.94% and 2.7%

respectively. Meher et al.³ recommended a single stage transesterification reaction (direct transesterification) with alkali catalyst when FFAs content are less than 3%. Thus, in the present study both the oils were transesterified in one step with alkali catalyst (NaOH). Moisture content was assumed to be very less and its effect was ignored.

All experiments have been carried out on a two liter batch reactor equipped with a fine tuned PID temperature controller. A constant temperature bath providing water for internal cooling, external heating jacket coil to maintain constant temperature and a motor drive to maintain the constant stirring rate for a particular set of the condition were used. The other specifications of the reactor were as follows

Maximum working temperature = 250°C

Maximum working pressure = 100 kg/cm²

Material of construction = SS316

Supply voltage = 220 V (single phase)

Table: 1 Schematic envisaged

Table: 1(a) For Linseed oil

T (°C)	Molar Ratio (alcohol: oil)	Catalyst (%w/w of oil)	Stirring (rpm)
40	6:01	0.5	750
50			
60	9:01	1.0	

Table: 1 (b) For Jatropha curcas oil

Molar Ratio (alcohol: oil)	Catalyst (%w/w of oil)	T (°C)	Stirring (rpm)
6 : 1	0.5	60	750
		50	
		40	300
		30	

Table: 2 Experimental conditions

EXPT	MR	Temp	Cat	rpm
Expt -1	6:01	40	0.5	750
Expt -2	6:01	40	1	750
Expt -3	9:01	40	0.5	750
Expt -4	9:01	40	1	750
Expt -5	6:01	50	0.5	750
Expt -6	6:01	50	1	750
Expt -7	9:01	50	0.5	750
Expt -8	9:01	50	1	750
Expt -9	6:01	60	0.5	750
Expt -10	6:01	60	1	750
Expt -11	9:01	60	0.5	750
Expt -12	9:01	60	1	750

EXPT	MR	Temp	Cat	rpm
Expt -1	6:01	0.5	60	750
Expt -2	6:01	0.5	60	300
Expt -3	6:01	0.5	50	750
Expt -4	6:01	0.5	50	300
Expt -5	6:01	0.5	40	750
Expt -6	6:01	0.5	40	300
Expt -7	6:01	0.5	30	750
Expt -8	6:01	0.5	30	300

Table: 2 (b) For Jatropha curcas oil

Table: 2(a) For Linseed oil

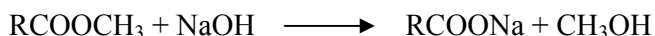
First linseed oil experiments were conducted to observe the transesterification reaction with different molar ratios, catalyst amounts and temperatures with constant stirring rate. The experiments planned for linseed oil are shown in Table 1 (a). The results were analyzed and the reaction conditions for *Jatropha curcas* transesterification reaction were set to different temperature and stirring rate and fixed molar ratio and amount of catalyst accordingly (Table 1(b)). All runs were repeated with the same reaction conditions and each sample was analyzed twice for ensuring the reproducibility of the data.

Estimation of methyl esters

The product of the transesterification reaction had two- upper (methyl esters) and bottom (glycerol) layers. These were different in color and density (0.872 and 1.26 respectively) and were easily separated using gravity settling method. After separation the upper layer (major constituent is methyl ester) was washed with lukewarm water (~70°C) to wash out the impurities (NaOH), unreacted methanol/alcohol and small fraction of bottom layer (mainly glycerol). The sample layer was kept in separating funnel for 8 hrs to get two different layers - washed methyl ester in the upper layer and waste material (milky color) in the bottom layer. The washing of the sample was repeated till the color of the bottom layer was observed to be same as the water used for washing to insure that there was no more NaOH. It was observed that three step washing (in each washing sample was left for 8 hrs) is sufficient to get the final washed sample. The final sample (upper layer) is used for the titration step and quantified in the term of conversion of TG and yield of methyl ester.

Ester content in upper layer was estimated by using modified titration method. This is based on the reaction between alkyl ester and sodium hydroxide in aqueous medium. The method as reported in the literature to estimate the esters is for “Volatile Esters in Cordials and Liqueurs”⁵³ - “Measure 100-500 ml sample into distg flask and steam distil as in AOAC Official Methods of Analysis, collecting volume distillate at least twice as great as volume of alcohol contained in the sample. Disconnect apparatus and wash out condenser with little H₂O. Add 1 ml phenolphthalein, and titrate to pink that persists greater than 1 min. using 0.1 N NaOH or KOH. Add measured excess of 25-50 ml 0.1 N alkali to solution, reflux for 1 hour, cool, and titrate excess alkali with 0.1 N H₂SO₄. Calculate number of 0.1 N alkali ml used in saponification of esters as EtOAc. 1 ml 0.1 N alkali equals 8.8 mg EtOAc.”⁵³

This method is used to estimate very small amount of esters present in cordials and liqueurs. The method is modified and used for estimation of methyl esters present in the upper layer of transesterification product mixture. The ester content is expectedly high in this mixture, approximately in range 60-90%. Therefore, 1 hour reflux time was not sufficient to quantify all the esters present in the samples. Thus, in the previous study by Kumar⁵⁴ experiments were started with a reflux time of one hour. The experiments were repeated with increased reflux time till a plateau was achieved (around 12 h) Thus, in this study, the reflux runs were carried out for 14 h. The neutralization reaction involved is given by



Results and Discussion

Equilibrium Conversion at different set of experimental conditions

Linseed oil

Transesterification reactions were carried out with linseed oil with different reaction conditions, depicted in Table 2(a). The effect of the different process variable, molar ratio,

temperature of the reaction and catalyst amount with fixed stirring rate were analyzed experimentally, an overall reversible kinetics mathematical model was developed and simulation runs were carried out.

One of the most important variables affecting the conversion of TGs is the molar ratio of alcohol to TGs. The stoichiometric molar ratio for transesterification is three moles of alcohol (e.g., methanol) to one mole of TGs, to produce three moles of alkyl esters (e.g., methyl esters) and one mole of glycerol. The effect of molar ratio on transesterification reaction is associated with the type of catalyst used. It is reported in open literature, acid-catalyzed transesterification requires a molar ratio of 30:1, while alkali-catalyzed reaction requires only 6:1 molar ratio to achieve the same equilibrium conversions.^{3, 27}

In the present study, the effects of two ratios (6:1 and 9:1) were investigated. Low molar ratios were considered since only alkali-catalyzed transesterification reactions with linseed oil were carried out. Figure 1 depicts the effect of molar ratio on the transesterification reaction at different conditions. It was observed that the equilibrium conversion increased with an increase in molar ratio. This is in agreement with theory (Le Chateliers principle). Approximately 1-3% increase in equilibrium conversions were observed with an increase in molar ratio from 6: 1 to 9:1. Error estimates were made and are reported in Figure 1.

The effects of three temperatures (40⁰C, 50⁰C and 60⁰C) on transesterification reaction have been investigated. The observed effects are reported in Figure 1. An increase in equilibrium conversion with an increase in temperature was observed as shown in Figure 1. Due to the sampling policy, the equilibrium conversions were observed between 30-45 min in all experiments. The equilibrium conversions at 40⁰C, 50⁰C and 60⁰C were observed to be approximately 88%, 91% and 93%, respectively (C = 0.5 % and M = 6:1). The equilibrium conversions achieved at 40⁰C, 50⁰C and 60⁰C were observed to be approximately 89%, 90% and 94%, respectively (C = 1% and M = 6:1). It was noted that the change in catalyst concentration does not affect the equilibrium conversions significantly. The equilibrium conversions achieved at 40⁰C, 50⁰C and 60⁰C were observed to be approximately 90%, 93% and 96%, respectively (C = 0.5 % and M = 9:1). The equilibrium conversions achieved at 40⁰C, 50⁰C and 60⁰C were observed to be approximately 90%, 94% and 96% respectively (for C = 1% and M = 9:1). Thus, it was observed that the equilibrium conversions increased approximately 2-3% for every 10⁰C rise in temperature. The equilibrium conversions also increased approximately 1-3 % with an increase in molar ratio.

The main role of catalyst in reaction kinetics is to reduce the activation energy. This reduction results in achieving equilibrium conversion in less time. Alkali-catalyzed transesterification are reported for vegetable oils with low free fatty acid content.²⁷ Thus, the transesterification of Linseed oil, in this study, was carried out with alkali-catalyst (NaOH). Two different concentrations, (0.5% and 1.0 % w/w of oil) of sodium hydroxide were used to study the effect of catalyst on transesterification. It was observed in all experiments that the equilibrium conversions were achieved between 30-45 min. Moreover, the equilibrium conversions were in the range of 88-96%. The experimental data are depicted in Figure. Each experiment was repeated and multiple estimations were done. Detailed error analysis was also done and is shown in Figure 1. It is to be noted that at any given condition, changing catalyst concentration has no significant effect on the equilibrium conversion. It is stressed that more data is needed at the initial stage of the transesterification to get a true observation and correct model. The samples collected otherwise predict a wrong model as shown in Figure 1.

***Jatropha curcas* oil**

The transesterification reaction data at four temperatures (30°C, 40°C, 50°C and 60°C) and different stirring rate (Table 2(b)) are reported in figures 2. The equilibrium is achieved between 30-40 min in all experiments. The equilibrium conversions at 750 rpm are observed to be approximately 53%, 63% 67% and 80% at 30°C, 40°C, 50°C and 60°C. Similarly, at 300 rpm they are observed to be 43%, 47%, 67% and 75%. Thus, it is observed that the equilibrium conversions increase with an increase in temperature. This is attributed to the fact that the equilibrium constant is increasing with an increase in the temperature in the reversible kinetics and thus the reaction is assumed to be endothermic.

Effect of stirring rates on the transesterification reaction kinetics is also studied. The observed data for different stirring speeds are reported in Figure 2. The equilibrium conversions are observed to be approximately 80% and 75% (at 60°C) and 53% and 43% (at 30°C) for 750 rpm and 300 rpm respectively. Similarly, it is observed that the equilibrium conversions are approximately 63% and 47% (at 40°C) for 750 rpm and 300 rpm, respectively. Thus, it is observed that the equilibrium conversions increase with an increase in stirring speed. Though, at 50°C an approximate equilibrium conversion of 67% was obtained at both 750 rpm and 300 rpm. The general trend of increase in equilibrium conversions with an increase in stirring rates can be attributed to two factors. Firstly, a high stirring rate helps in immediate formation of emulsion (between oil and methanol) and also results in small drop sizes. This leads to rapid conversions as observed in Figure 2. Secondly, it is assumed that high stirring rate shifts the reaction from a mass transfer controlled region at low stirring rate to a chemical reaction controlled region at high stirring rates. This observation is in accordance with the observed values of the activation energies.

Mathematical modeling and simulation

Several kinetic studies are reported to observe the effects of operating conditions on the final yield of biodiesel (or the final conversion of TG) in batch transesterification reactors. The transesterification reaction is a reversible reaction, and proceeds in three consecutive steps. The overall reaction, assumed to be a single step (ignoring/ neglecting intermediate steps), was considered to develop a kinetic rate equation. This rate equation has six unknown parameters (four order of the reaction with respect to two reactants and two products each and two rate constants for forward and backward directions).

In the present work, an overall reversible kinetics mathematical model has been developed to fit the experimental values. ‘Gear’s technique’⁵⁵ was adopted to solve the rate equation (initial value problem) at different time to generate the data for conversion v/s time. ‘Genetic Algorithms’⁵⁶ (GA) was applied to minimize the error between experimental and model generated conversion values. The optimal best fit values of unknown parameters were used to find the Arrhenius dependency and calculation of activation energies and the order wrt reactants and products.

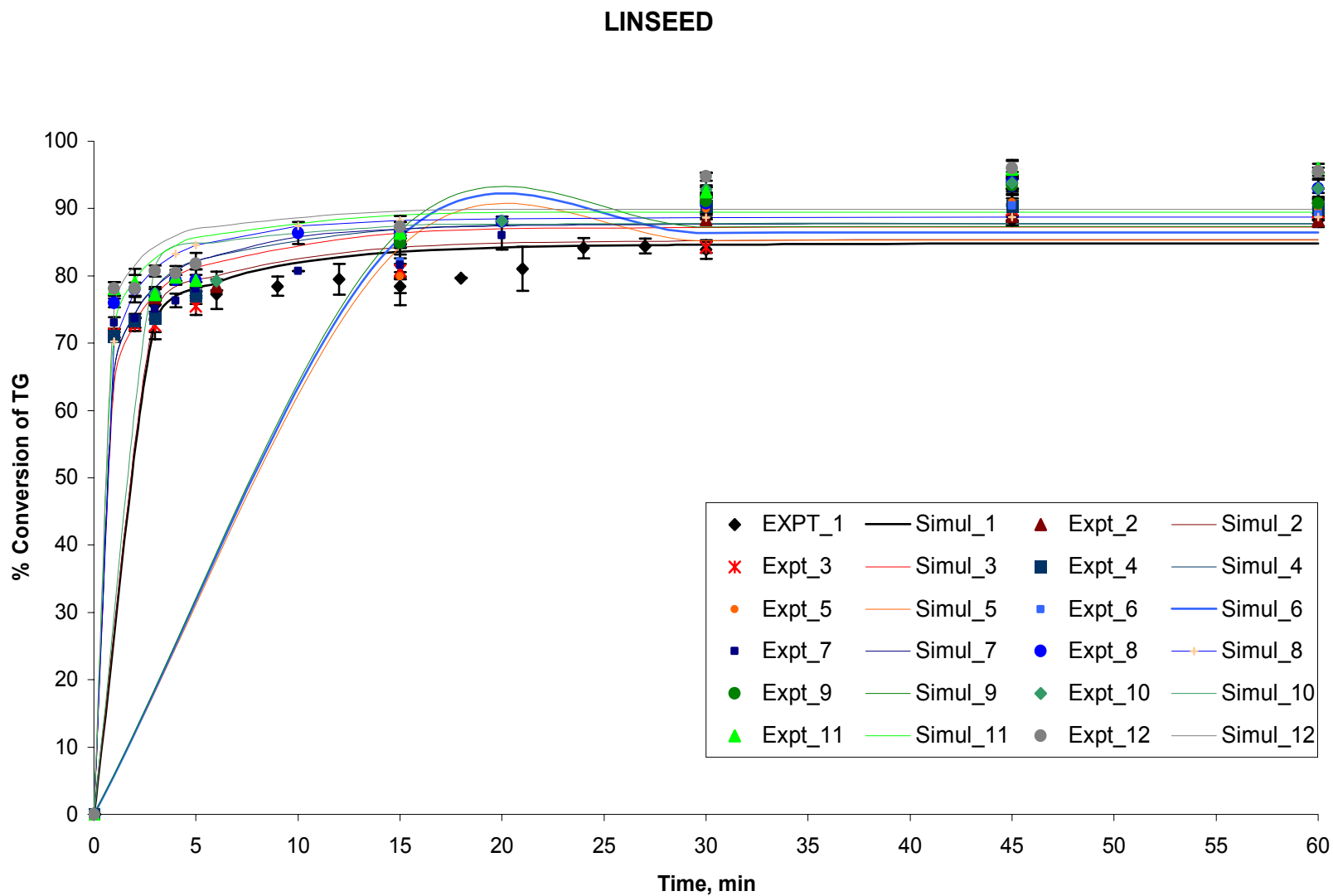


Figure: 1 Experimental (discrete points) and simulation (continuous line) for Linseed Methyl Ester

JATROPHA CURCAS

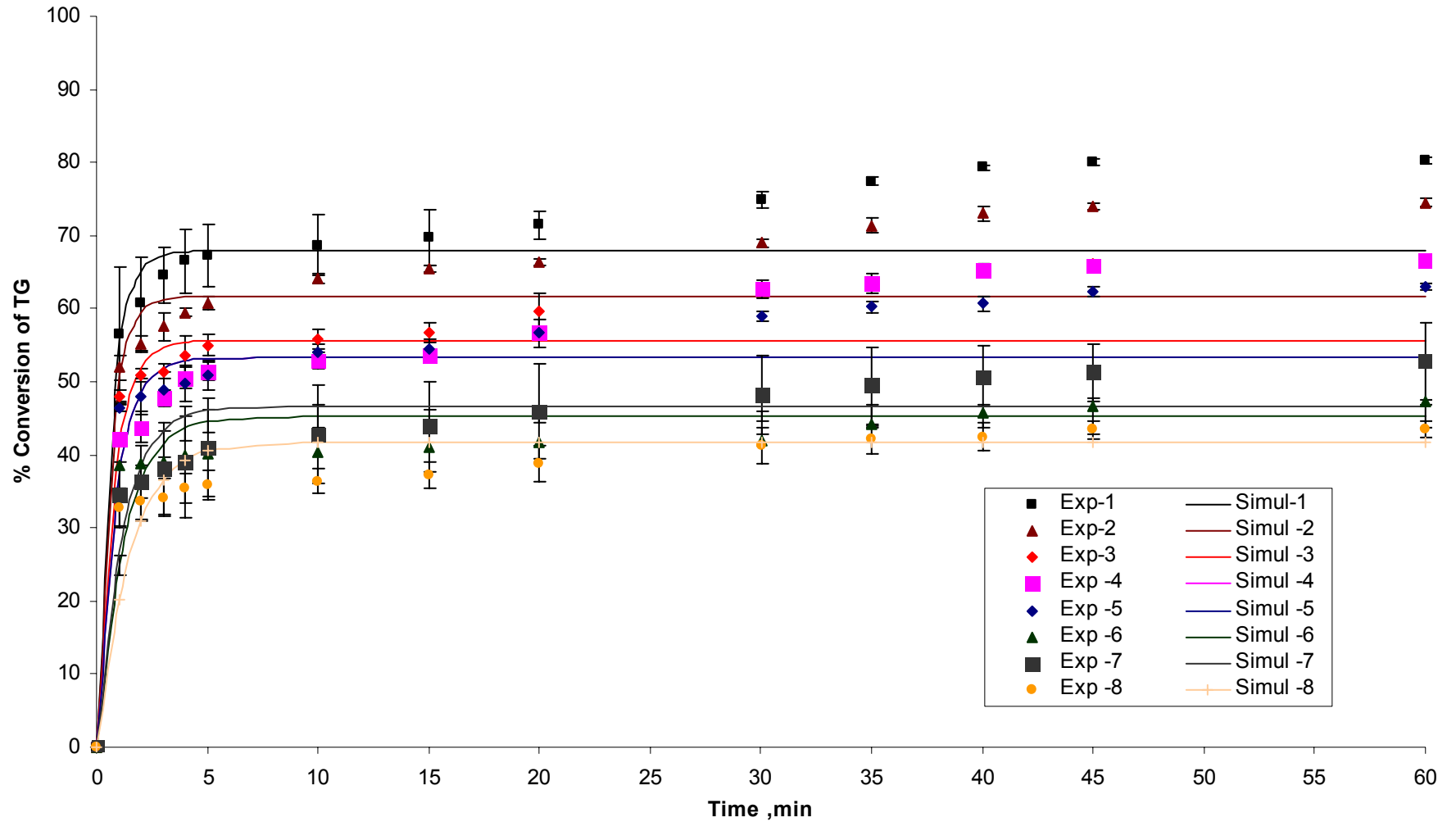


Figure: 2 Experimental (discrete points) and simulation (continuous line) for Jatropha Methyl Ester

Kinetic results

Kinetic studies for transesterification of biodiesel production from both feedstock oils were performed on the basis of optimum values of the unknown variables of the rate equations.

Linseed oil

The optimum values of the unknown variables of the rate equation were evaluated. The orders of the reaction with respect to each component were observed to be: TG ($a = 2.97$), methanol ($b = 1.29$), linseed methyl ester ($c = 1.94$) and glycerol ($d = 0.25$). Best fit between the experimental and model predicted values for linseed transesterification were observed for these optimal values. Forward (k_1) and backward (k_2) rate constants and overall rate constants (K) and activation energies (E_a) for different conditions were estimated and are given in Table 3. In Figure 1 the curves (Exp5, 6 and 9) are not following the trend in the absence of initial data. Thus to get the same trend for initial time period, some initial data are required. Although, the reaction rate parameters are screening the homogeneity.

MR and C%	6:1 and 0.5%			6:1 and 1%			9:1 and 0.5%			9:1 and 1%		
T	k ₁	k ₂	K	k ₁	k ₂	K	k ₁	k ₂	K	k ₁	k ₂	K
313.15	0.6124	0.001	471	0.698	0.0013	537	0.612	0.0013	471	0.698	0.0013	537
323.15	0.6942	0.001	534	0.9762	0.0014	697	0.694	0.0013	534	0.9762	0.0014	697
333.15	1.154	0.001	888	1.4947	0.0015	996	1.154	0.0013	888	1.4947	0.0015	996
1/T	lnk ₁	lnk ₂	lnK	lnk ₁	lnk ₂	lnK	lnk ₁	lnk ₂	lnK	lnk ₁	lnk ₂	lnK
0.003193358	-0.4904	-6.645	6.16	-0.3595	-6.6454	6.29	-0.49	-6.6454	6.16	-0.3595	-6.6454	6.29
0.003094538	-0.365	-6.645	6.28	-0.0241	-6.5713	6.55	-0.36	-6.6454	6.28	-0.0241	-6.5713	6.55
0.003001651	0.1432	-6.645	6.79	0.4019	-6.5023	6.9	0.143	-6.6454	6.79	0.4019	-6.5023	6.9
R = 1.98 cal/(mol Kelvin)												
Slope	-3283.4			-3219.4			-3283.4			-3219.4		
E_a kcal/mol	6.501132			6.374412			6.501132			6.374412		
K ₀	1.58E+07			1.54E+07			1.58E+07			1.54E+07		
R ²	0.8801			0.9886			0.8801			0.9886		

Table: 3 Rate constants and Activation energies for Linseed oil with constant stirring rate (750 rpm).

Jatropha oil

Stirring rate	750 rpm			300 rpm		
Temp	k ₁ (0.1-3.0)	k ₂ (0.001-0.1)	K	k ₁ (0.1-3.0)	k ₂ (0.001-0.1)	K
303.15	0.46	0.2	2.3	0.31	0.2	1.55
313.15	0.78	0.2	3.9	0.41	0.2	2.05
323.15	0.95	0.2	4.75	0.78	0.2	3.90
333.15	0.95	0.2	4.75	1.45	0.19	7.63
1/T	lnk ₁	lnk ₂	lnK	lnk ₁	lnk ₂	lnK
0.0032987	-0.77653	-1.60943791	0.832909123	-1.171183	-1.609437912	0.43825493
0.00319336	-0.24846	-1.60943791	1.360976553	-0.8915981	-1.609437912	0.71783979
0.00309454	-0.05129	-1.60943791	1.558144618	-0.2484614	-1.609437912	1.36097655
0.00300165	-0.05129	-1.60943791	1.558144618	0.37156356	-1.660731207	2.03229476
Activation energy	E _a = 4.808 Kcal /mol			E _a = 10.792 kcal /mol		

Table: 4 Rate constants and Activation energies for Jatropha curcas oil (MR 6:1 and 0.5% catalyst)

The reaction orders with respect to reactants and products (a, b, c and d) were observed to be 2.0, 0.0, 1.0 and 1.0 respectively. These are the optimum value, which gave the best fit between the experimental and model predicted values for *Jatropha curcas* transesterification process. Forward (k_1) and backward (k_2) rate constants and overall equilibrium constant (K) and overall activation energies for different conditions were estimated as given in Table 4.

Biodiesel as Fuel

Some fuel properties like density, kinematic viscosity, flash point, cloud and pour point were estimated using standard techniques specified by ASTM and these properties were compared with diesel fuel and ASTM D6751 standard values for biodiesel, for both linseed methyl ester and *Jatropha* methyl ester. These values are in the close range and favor the biodiesel produce from non edible oil (Linseed and *Jatropha curcas*) to use as a fuel.

Properties	Methyl Ester (BD)		ASTM Standards	
	Linseed	Jatropha	Biodiesel ⁴⁸	Diesel ⁴⁸
Density (30 ⁰ C)	0.852	0.88698		0.855
K. Viscosity(30 ⁰ C)	3.95	6.08	1.9-6.0	1.9-4.1
Flash Point, ⁰ C	151	97	100	76
Cloud point, ⁰ C	3.17	11.5	-	-
Pour point, ⁰ C	-6.25	9.5	-	-16

Table: 5 Fuel properties

Conclusions

The effect of operating conditions on the kinetics of the transesterification reaction of vegetable oils, Linseed and *Jatropha curcas*, to produce biodiesel were studied.

Linseed oil

The orders of the reaction were found to be 2.97, 1.29, 1.94 and 0.25 for TG, methanol, methyl ester and glycerol, respectively. The equilibrium constant in all simulations were observed to increase with an increase in temperature indicating that alkali-catalyzed transesterification reaction is endothermic. It was also observed that equilibrium conversions increased with an increase in temperature. For endothermic reversible reactions, activation energy for forward reaction is more than that for backward reaction. The activation energies for both reactions were estimated. The overall activation energies were estimated in the range of 6.30-6.5 kcal/mol. The rate constants were also found to increase with an increase in temperature and catalyst concentrations.

Simulations were done to predict the reversible kinetics for all experimental conditions for which experimental data were collected. Model fitnesses were observed to be more than 0.97. Effects of varying parameters like temperature, catalyst concentrations and molar ratio were studied in simulations. Similar effects were found in simulations and actual experimental studies. It was observed that increasing temperature resulted in

increased rate of reaction and equilibrium conversions. No significant effect was observed, both in simulations and experimental data, with an increase in catalyst concentration from 0.5 % to 1.0 %. It was observed that increasing molar ratio resulted in an increase in TG conversions (X_A). Moreover, the equilibrium conversions were achieved in less time with an increase in molar ratios. It was also observed that the percentage increase in equilibrium conversion for molar ratio larger than 12:1 molar ratio were insignificant. Thus, the model developed was observed to be strong enough to predict the effect of these parameters on reaction kinetics.

Jatropha oil

It is observed that the time required in reaching the equilibrium conversions and the equilibrium conversions both were dependent on temperature and stirring rates. The equilibrium conversion was more sensitive to temperature and stirring rates, and increased with an increase in these variables. The time required to reach the equilibrium was less sensitive to these changes and decreased with an increase in temperature and stirring rates. The maximum equilibrium conversion was obtained for 60°C and 750 rpm. The dependency of equilibrium constant on temperature followed the standard Arrhenius trend for an endothermic reversible reaction. The TG conversions for *Jatropha* achieved were less compared to Linseed oil at the same set of the condition. This is attributed to the fact that high FFAs are present in *Jatropha curcas* compared to Linseed. Overall, different kinetics toward equilibrium conversions were observed with both the oils studied but the overall trends were observed to be similar.

Acknowledgement

Authors would like to thank Dr. A K Agarwal for initiating them in this field. This work was partially supported by a research grant from *Khadi and Village Industries Commission* (KVIC), Government of India, to Dr. A K Agarwal and Dr. S Garg.

References

1. Raheman H, Phaveatare AG. Diesel Engine Emission and Performance from Blends of Karanja Methyl Ester and Diesel. *Biomass and Bioenergy*. 2004;27: 393-397.
2. Szybist JP, Boehman AL, Taylor JD, McCormick RL. Evaluation of formulation strategies to eliminate the biodiesel NOx effect. *Fuel Processing Technology*. 2004; Article In Press.
3. Meher LC, Sagar DV, Naik SN. Technical Aspect of Biodiesel Production by Transesterification- A Review. *Renewal and Sustainable Energy Reviews*. 2006; 10: 248.
4. Barnwal BK, Sharma MP. Prospects of Biodiesel Production from Vegetable Oils in India. *Renewable and Sustainable Reviews*. 2005; 9: 363.
5. Srivastava A, Prasad R. TGs-based Diesel Fuels. *Renewable and Sustainable Energy Reviews*. 2000; 4: 111.
6. Subramanian KA, Singal SK, Saxena M, Singhal S. Utilization of Liquid Biofuels in Automotive Diesel Engines: An Indian Perspective. *Biomass and Bioenergy*. 2005;29(1): 65.

7. Szybist JP, Boehman AL, Taylor JD, McCormick RL. Evaluation of Formulation Strategies to Eliminate the Biodiesel NO_x Effect. *Fuel processing Technology*. 2005;86 (10):1109.
8. Carreretto C, Macor A, Mirandola A, Stoppato A, Tonon S. Biodiesel as Alternative Fuel: Experimental Analysis and Energetic Evaluations. *Energy*. 2004, 29, 2195.
9. Sinha S, Agarwal AK. Performance Evaluation of a Biodiesel (Rice Bran Oil Methyl Ester) Fuelled Transport Diesel Engine. *SAE International*. 2005; 1: 1730.
10. Ma F, Hanna MA. Biodiesel Production: a review. *Bioresource Technology*. 1999; 70: 1-15.
11. Khan AK, Kinetics and Catalyst Development. Thesis submitted to Department of Chemical Engineering, the University of Queensland (Brisbane), Australia, 2002.
12. Sudha P, Ravndranath NH. Land Availability and Biomass Potential in India. *Biomass and Bioenergy*. 1999; 16: 207.
13. Subramanian KA, Singal SK, Saxena M, Singhal S. Utilization of Liquid Biofuels in Automotive Diesel Engines: An Indian Perspective. *Biomass & Bioenergy*. In Press, 2005.
14. Anon. Wealth of India, Raw Materials; Council of Scientific and Industrial Research: New Delhi:1959.
15. Freedman B, Butterfield RO, Pryde EH. Transesterification Kinetics of Soybean Oil. *Journal of American Oil and Chemist Society*. 1986; 63(10): 1375.
16. Wimmer T. Transesterification Process for Preparation of C-15 Alkyl Fatty Esters from Fatty Glycerides and Monovalent Lower Alcohols. *PCT Intl. WO*. 1992: 9200.
17. Ramadhas AS, Jayaraj S, Muraleedharan C. Biodiesel Production From High FFA Rubber Seed Oil. *Fuel*. 2005; 85 (4): 335.
18. Chitra P, Venkatachalam P, Sampathrajan A. Optimisation of Experimental Conditions for Biodiesel Production form Alkali Catalyzed Transesterification of *Jatropha curcus* Oil. *Energy for Sustainable Development*. 2005 ; 9(3): 13.
19. Meher LC, Vidya SS, Naik SN. Optimization of Alkali Catalyzed Transesterification of *Pongania pinnata* for Production of Biodiesel. *Bioresource Technology*. 2006; 97 (12): 1392.
20. Feuge RO, Grose T. Modification of Vegetable Oils. via. Alkali Catalyzed Interesterification of Peanut Oil with Ethanol. *Journal of American Oil and Chemist Society*. 1949; 26: 97.
21. Dorado MP, Ballesteros E, Almeida JA, Schellet C, Lohrlein HP, Krause R. An Alkali Catalyzed Transesterification Process for High Free Fatty Acid Oils. *ASAE* . 2002; 45(3): 525
22. Canakei M, Gerpen JV. Biodiesel Production via Acid Catalysis. *American Society of Agricultural Engineers*. 1999; 42(5): 1203.
23. Zullaikah S, Lai CC, Ramjan S, Ju YH. A Two Step Acid Catalyzed Process from Rice Bran Oil. *Bioresource Technology*. 2005; 96 (17): 1889
24. Ma F, Clements LD, Hanna MA. The Effect of Mixing on Transesterification of Beef Tallow. *Bioresource Technology*. 1999; 69: 289.
25. Turck R. Method for Producing Fatty Acid Esters of Monovalent Alkyl Alcohols and Use Thereof. *USP 0156305*. 2002.
26. Freedman B, Butterfield, RO, Pryde EH. Transesterification Kinetics of Soybean Oil *Journal of American Oil and Chemist Society*. 1986; 63(10): 1375.

27. Tomasevic AV, Marinkovic SS. Methanolysis of Used Frying Oils. *Fuel Process Technology*. 2003; 81: 1.
28. BradshawGB, Meuly WC. Preparation of Detergents. US Patent 2. 1944: 360
29. Nye MJ, Southwell PH. Esters from Rapeseed Oil as Diesel Fuel. In: *Proceedings of Vegetable Oil as Diesel Fuel Seminar III*. Peoria: Northern Agricultural Energy Center.1983: 78.
30. Freedman B, Pryde EH, Mounts TL. Variables Affecting the Yield of Fatty Esters from Transesterified Vegetable Oils. *Journal of American Oil and Chemist Society*. 1984; 61(10): 1638.
31. Tanaka Y, Okabe A, Ando S. Method for the Preparation of a Lower Alkyl Ester of Fatty Acids. US Patent 4. 1981:303.
32. Ali Y. Beef Tallow as a Biodiesel Fuel. PhD dissertation. Biological Systems Engineering, University of Nebraska, Lincoln. 1995.
33. Edger L, Yijun L, Dora EL, Kaewta S, David AB, Ghoodwin JG. Synthesis of Biodiesel via Acid Catalyst. *Industrial Engineering and Chemistry Research*. 2005;44: 5353.
34. Ahn E, Mittelbach M, Mar RA. Low Waste Process for the Production of Biodiesel. *Separation Science and Technology*. 1995; 30(7): 2021.
35. Gemma V, Mercedes M, Aracil J. Integrated Biodiesel Production: A Comparison of Different Homogeneous Catalysts System. *Bioresource Technology*. 2004; 92: 297.
36. Gryglewicz S, Rapeseed Oil Methyl Esters Preparation using Heterogeneous Catalysts. *Bioresource Technology*. 1999; 70: 249.
37. Galen JS, Mohanprasad A, Eric JD, Pratik JM, Michael JG. Transesterification of Soybean Oil with Zeolite and Metal Catalysts. *Applied Catalyst A: General*. 2004; 257: 213.
38. Kim HK, Kang B, Kim MJ, Park YM, Kim D, Lee J, Lee K. Transesterification of Vegetable Oil to Biodiesel using Heterogeneous Base Catalyst. *Catalysis Today*. 2004; 93: 315.
39. Frederique RA, Daniella GL, Elias HH, Carlos W, Paulo AZS. Utilization of Metal Complexes as Catalysts in the Transesterification of Brazilian Vegetable Oils with Different Alcohols. *Journal of Molecular Catalysis A : Chemical*. 2004; 209: 29.
40. Mohamad IW, Ali OA. Evaluation of the Transesterification of Waste Palm Oil into Biodiesel. *Bioresource Technology*. 2002;85: 25.
41. Fuduka H, Kondo A, Noda H. Biodiesel Fuel Production by Transesterification of Oils. *Journal of Bioscience and Bioengineering*. 2001; 92(5): 405.
42. Mohamed MS, Bornscheuer WT. Improvement in Lipase Catalyzed Synthesis of Fatty Acid Methyl Esters from Sunflower Oil. *Enzyme and Microbial Technology*. 2003;33: 97.
43. Watanabe Y, Shimada Y, Sugihara A, Noda H, Fukuda H, Tominaga, Y. Continuous Production of Biodiesel Fuel from Vegetable Oil using Immobilized *Canadia Antactica* Lipase. *Journal of American Oil and Chemist Society*. 2000; 77: 355.
44. Shweta S, Sharma S, Gupta MN. Biodiesel Preparation by Lipase-Catalyzed Transesterification of *Jatropha* Oil. *Energy & Fuels*. 2004; 18(1): 154.
45. Iso M, Chen B, Eguchi M, Kudo T, Shrestha S. Production of Biodiesel Fuel from TGs and Alcohol using Immobilized lipase. *Journal of Molecular Catalysis B: Enzymatic*. 2001; 16: 53.

46. Nouredini H, Gao X, Philkana RS. Immobilized *Pseudomonas cepacia* lipase for Biodiesel Fuel Production From Soybean Oil. *Bioresource technology*. 2005; 96: 769.
47. Smith MK. Process of Producing Esters. U S patent. 1949; 2: 444.
48. Gerpan JV, Clements D, Knothe G. Biodiesel Production Technology: Subcontractor Report: NREL. 2004.
49. Boocock DG, Konar SK, Mao V, Sidi H. Fast One-Phase Oil-Rich Processes for the Preparation of Vegetable Oil Methyl Esters. *Biomass and Bioenergy*. 1996; 11: 43.
50. Boocock DG, Konar SK, MaoV, Lee C, Bulugan S. Fast Formation of High-Purity Methyl Esters from Vegetable Oils. *Journal of American Oil and Chemist Society*. 1998; 75(9): 1167.
51. Boocock DG. Single Phase Process for Production of Fatty Acid Methyl Esters from Mixtures of TGs and Fatty Acids. WO 0112581. 2001.
52. Boocock DG. Process of Producing Lower Alkyl Fatty Acid Esters. CA 0112581. 1996.
53. Oils and Fats. AOAC Official Methods of Analysis. 1984.
54. Kumar R. Experimental Studies, Modeling and Simulation of Linseed Oil Transesterification of Biodiesel Production. M. Tech. dissertation Thesis. IIT Kanpur, India.
55. Gupta SK. Numerical Methods for Engineers; Wiley Eastern Limited: New Delhi:1995.
56. Deb K. Optimization for Engineering Design; Prentice Hall of India: New Delhi: 2003.