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Catalysis in biodiesel formation

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Abstract
Fossils fuels are main source of energy but these are not renewable so after a time these may disappear so renewable sources of energy were used such as solar energy hydro energy. Energy from biomass. Biodiesel is also used as energy source in transportation because it is manufactured from vegetable and animal oils by transesterification reaction using homogeneous and heterogeneous catalyst and also from acid and base hydrolysis mixture of used cooking oils and methanol. Biodiesel is renewable as well as biodegradable and causes less pollution to our environment. Ultrasonic technology and co-solvent (mainly non-polar) were also used to increase the mass transfer between two phases of immiscible liquid of methanol and oil.

Keywords: Catalysis, biodiesel, transesterification

Introduction
Catalyst is a substance which modified the rate of reaction, and this phenomenon is called catalysis. If a catalyst increases the rate of reaction then it is called positive catalyst if it decreases the rate of reaction then these are called inhibitor and also known as negative catalyst. Catalyst modified the rate of reaction only by changing the activation energy (fig.1) and these don't affect thermodynamic properties such as equilibrium constant and Gibbs free energy which are related to spontaneity of the reactions. Catalyst are majorly of two types homogeneous and heterogeneous. When catalysts are used in biological system then these are called enzymes. Enzymes are mostly proteins made up of amino acid.

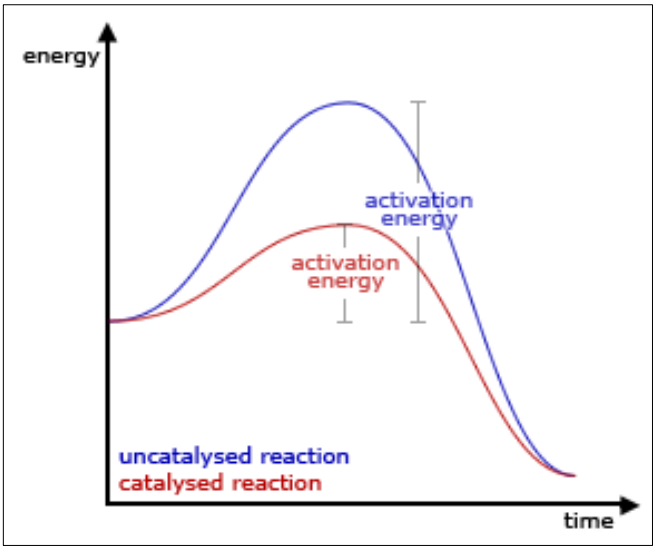
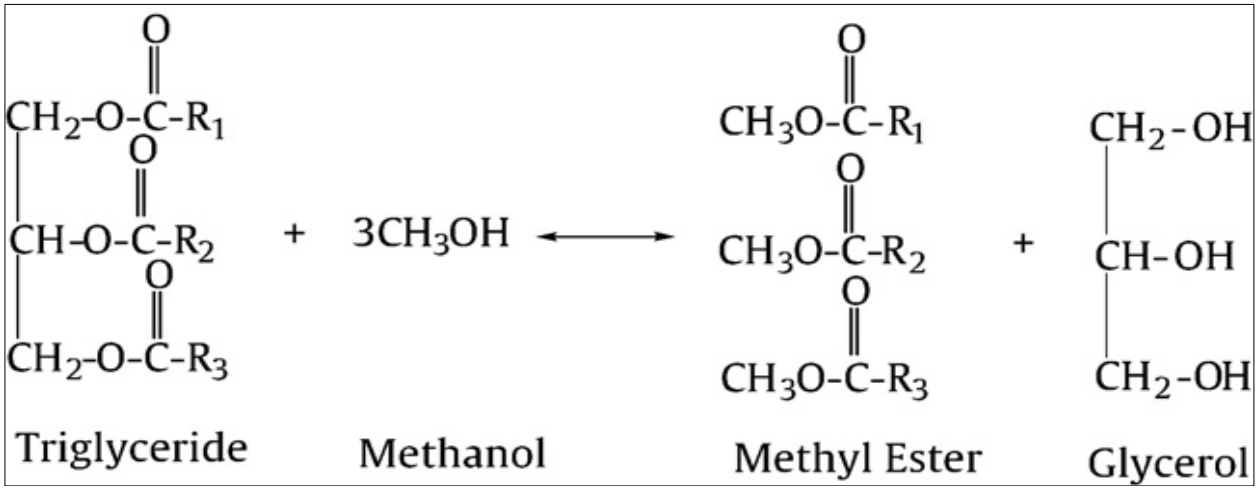


Fig 1: Energy diagram of a reaction with and without catalyst.

According to International Energy Agency I, 2006 primary source of energy in our day to day life is fossil fuels out of which 57.7% of used in transportation. Fossils fuels is mainly made up of hydrocarbons. Approx. 934 million tones diesel is used in one year. If we consumed fossils fuels in that speed then it is consumed and we have to face problem of fuels in nearby 10-15 upcoming years. So renewable energy sources or fuels should be made available so that this problem will b sorted.

Now a day a number of renewable sources are studied such as solar energy, hydro energy, energy from biomass, fuel cells which converts energy with high efficiency and low emission. for transportation purposes an alternative to diesel is biodiesel which is biodegradable, renewable and non-toxic. Biodiesel is mainly made up from vegetable oil and animal oil. Vegetable and animal oils are mainly esters of fatty acid and glycerol. Different properties of these oils are due to different properties of fatty acids. These acids are less volatile and viscous so these may not used as such for fuels because of their high viscosity. If these were used in fuels they may cause chocking and ring sticking in engine. Therefore, to use them as fuels these must be modified by some chemical reactions then these are called biodiesel. Biodiesel are prepared from this by simply cracking or pyrolysis but these are complicated processes and a number of side products. So, biodiesel prepared by transesterification of vegetable and animal oils which reduces their viscosity. In these reaction fatty acid and methyl esters are obtained from acid and base hydrolysis of triglycerides and methanol. Glycerol is a side product in these reactions.



Biodiesel is mainly mixture of fatty acid and alkyl ester mainly methyl esters (FAME) if methanol is used just because methanol is easily available and cheap. Due to different composition of FAME biodiesel is characterized. In this paper it is reported that how catalyst is used in biodiesel formation.

Preparation of Biodiesel

Currently 154 million tonnes of cooking oil were produced globally. Cooking oil is mainly made up of vegetable and which is used for frying purposes. After using it for cooking purposes it was disposed if proper care is not taken for its disposing then it may contaminant water which causes adverse effects to human beings.

Table 1: Composition in % of fatty acid in different cooking

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic	0.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3.0
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	10.7	2.2
Linolenic	8.6	0.6	0.2	0.4	0.4	0.0

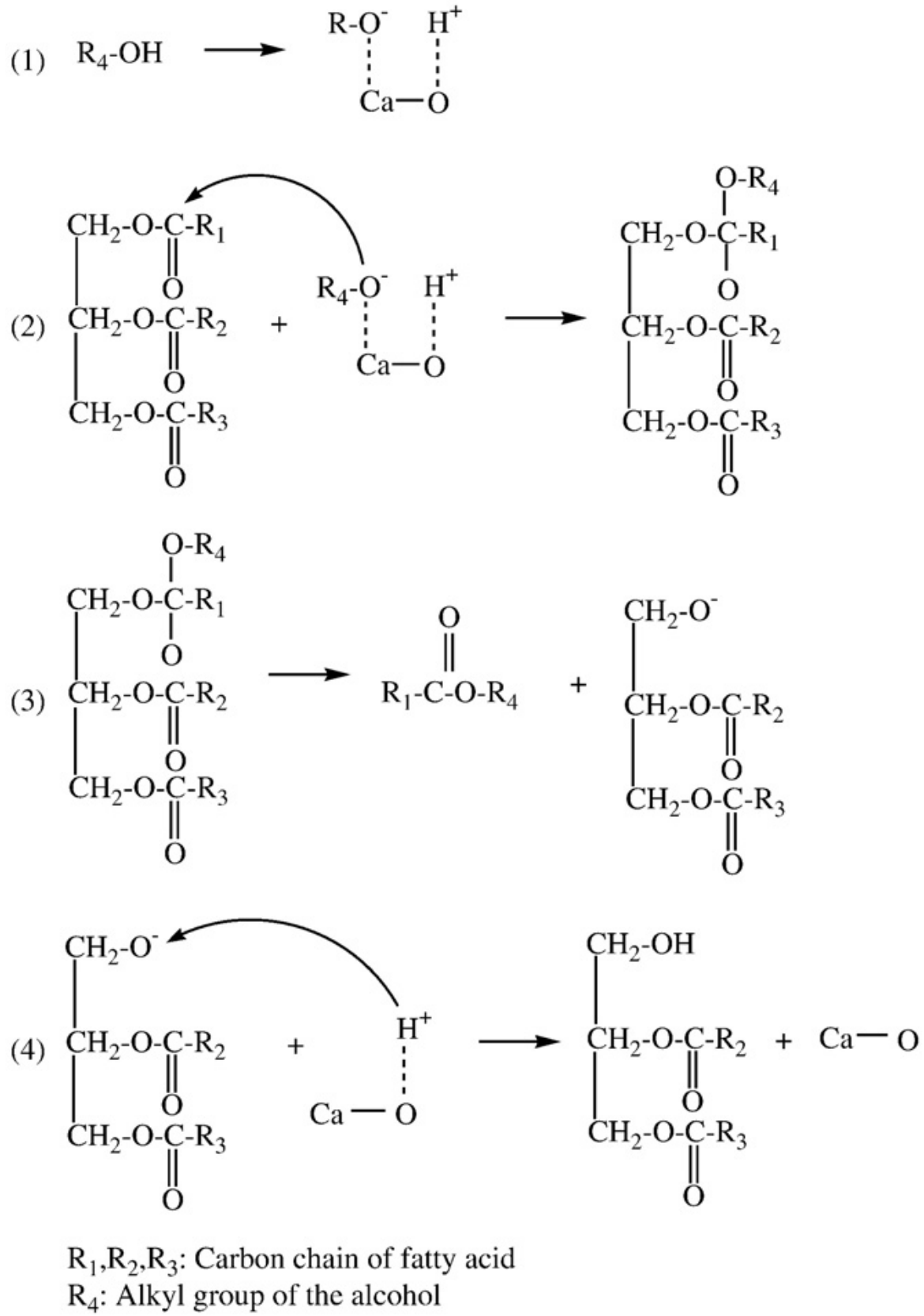
In frying process of cooking mainly oil is heated at high temperature for a long time due to this there occurs some physical changes in oils such as increase in viscosity and specific heat and change in surface tension and color. Mainly three types of reaction occur which are thermolytic, oxidative and hydrolytic.

Used cooking oil is used as a feedstock for obtaining biodiesel because in this quantity of free fatty acid increases then normal refined oil. In thermolytic reaction oil is heated in absence of oxygen which produce hydrocarbons, CO, CO_2, fatty acid etc. In oxidative reaction oxygen is supplied while heating and produced hydrocarbons, lactones, alcohols, acids, esters and saturated and unsaturated aldehydes and ketones. During cooking steam is produced which is used for hydrolytic of oils and gives fatty acid, glycerol and mono and diglycerides.

Transesterification by acid and bases (Homogeneous catalysis)

Transesterification of waste cooking oil is done by catalysis mainly heterogeneous and enzymes. Homogeneous catalysts mainly acid and base are used to obtain biodiesel from feedstock. Leung and Guo (2006) [7] studied the hydrolysis of mixture of methanol and waste cooking oil (6:1) using NaOH and obtained biodiesel with 88.8% yield. 9:1 methanol and waste cooking oil were hydrolyzed by KOH and biodiesel was obtained. H_2SO_4 was used to acid hydrolyzed mixture of methanol and waste cooking oil at different temperature for better yield of biodiesel. Wang *et al.* (2006) [9], Patil *et al.* (2010) [11] and Wan Omar *et al.* (2009) [12] studied the two-step acid base hydrolysis. In this first hydrolysis is done in presence of acid then in presence of base in presence of ferric sulfate which enhances the yield of biodiesel.

The mechanism of two step acid base hydrolysis was shown as:



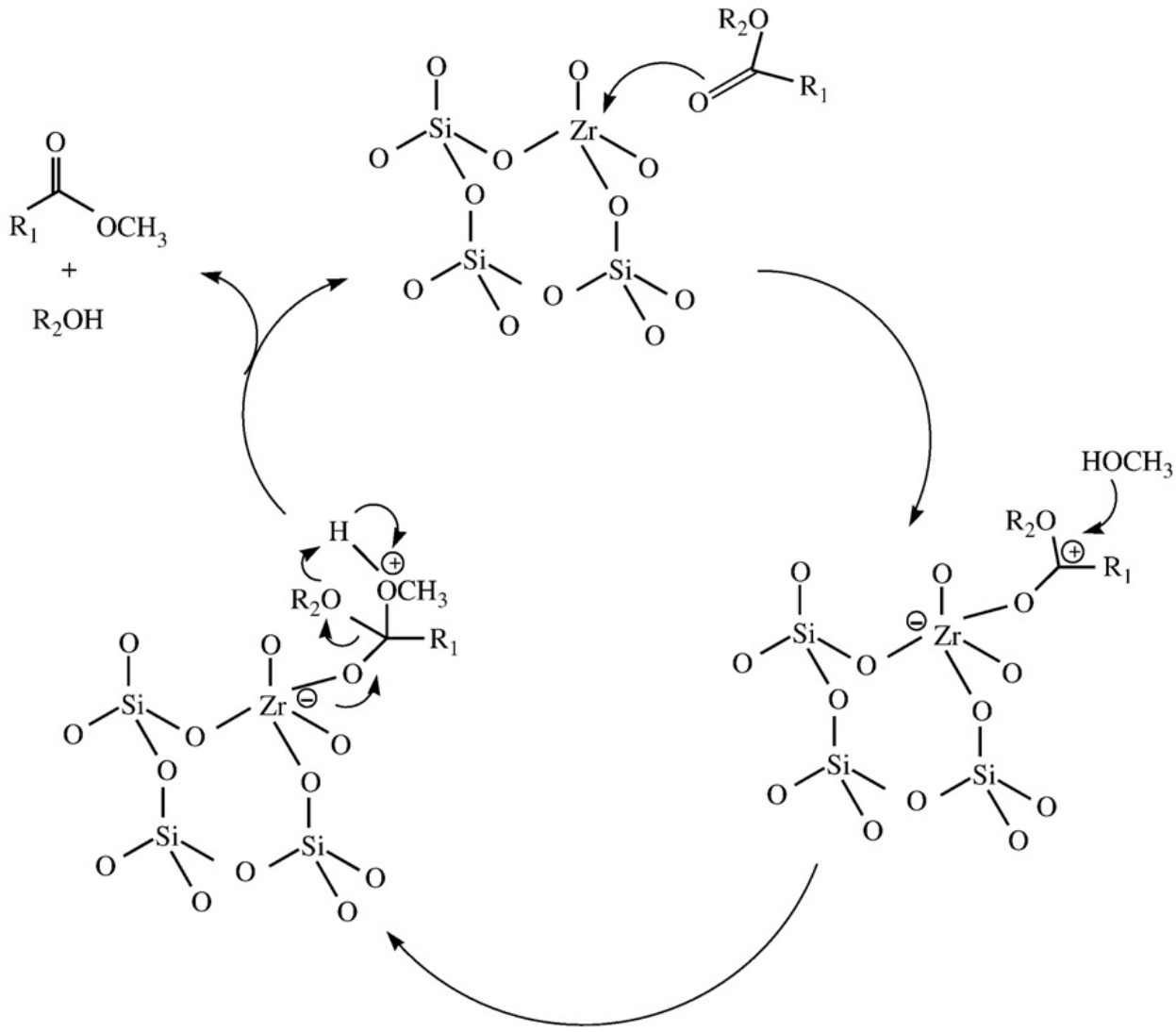
R_1,R_2,R_3: Carbon chain of fatty acid
R_4: Alkyl group of the alcohol

Heterogeneous catalysis

Heterogeneous catalysis is in which reactants, products are in same phase and catalyst are in different phase mainly solid catalyst are used in heterogeneous catalysis. Kouzu *et al.* (2008) prepared biodiesel by refluxing mixture of methanol and waste cooking oil in (12:1) by using CaO as catalyst. When methanol and wasted cooking oil (6:1) is heated in presence of K_3PO_4 as a catalyst biodiesel obtained with a tremendous yield 97.6%.

Obtained the biodiesel from methanol sand oleic acid (19.4:1) using WO_3/ZrO_2 which are acidic in nature. Many zeolites and mixed metallic clustered compounds were used as catalyst to obtain biodiesel from the mixture of methanol and used cooking oil with different molar ratios.

Mechanism of formation of biodiesel using ZrO_2 as heterogeneous catalysis is shown as:



R_1,R_2: Carbon chain of fatty acid
Zr: Zirconia, Si: Silica

Enzymes Catalysis

Enzymes are biocatalyst which are mainly used in biochemical reactions but these are also used to oobtain biodiesel from the mixture of methanol and used cooking oil. Example of some enzymes are which are used for these purposes are as Candida Antarctica (Novozym 435), Pseudomonas cepacian (PS 30), Novozym 435, Rhizopus oryzae, Immobilized Penicillium expansum on resin D4020 etc.

Ultrasonic technology in transesterification reaction

To increase mass transfer rate between immiscible liquid–liquid phases within a heterogeneous system ultrasonic waves (the sound waves which are beyond the rich of human ears, human ears mainly responsds the sound which have frequency between 16 and 18 kHz,) are used. Ultrasonic waves have frequency between 20 kHz and 100 MHz. ultrasonic technology is widely used in various biological and chemical reactions to improve the yield and to short the time period of that reaction. The higher frequency ultrasonic waves create distortion in chemical compounds this may causes stretching or compressing of bond. Due to these radiation, vibration also occurred and which causes chemical and mechanical defects are obtained which may disrupts the energy of a system and due to this phase boundary collapse and thus two immiscible liquid are mixed and thus there occurs a chemical reaction between them. Ultrasonic waves provide sufficient energy to dissolve so that transesterification occurred sand also provide efficient amount of activation energy so that reaction completes faster than usual. Ultrasonic waves not only decreases the time of reaction but also reduces the ratio of methanol and oil show that it can act as better fuels.

Effect of co-solvent in transesterification

Non-polar compounds such as tetrahydrofuran (THF), dimethyl ether, hexane etc. are used in transesterification reaction as co-solvent because transesterification is slow reaction it takes normally 20 minutes just because the reactants alcohol and oils are not miscible in each other. So to accelerate a reaction its reactants should be dissolved so that these are used as a co-solvent to increases the rate of reaction and also for better yield. One more advantage of using non-polar solvents as co-solvent in transesterification reaction is that these can be easily separated from methanol because methanol is used in excess in these reactions. Co-solvent are used in both heterogenous and homogeneous catalysis but in heterogeneous catalysis of biodiesel formation from used cooking oil and methanol decreases the yield of the reaction.

So co-solvent are mainly used in homogeneous catalysis in heterogeneous then don't participate in mass transfer between two phase.

Conclusion

Fossils fuels are nonrenewable and causes pollution to our environment so alternative of these are used as source of energy which are renewable and causes no or less pollution to environment. So, in this biodiesel is great alternative as a fuel in transportation. It is prepared from used cooking oil used as feedstock in methanol using acids, bases, catalyst heterogenous and homogenous both. Biodiesel is also formed from enzymatic transesterification of used cooking oil. Ultrasonic technology and cosolvent such as THF, dimethyl ether etc. are used to enhance the rate of transesterification of reaction by increasing the mass transfer between two phases.

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