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Transesterification of triglycerides using heterogeneous catalysts: A review

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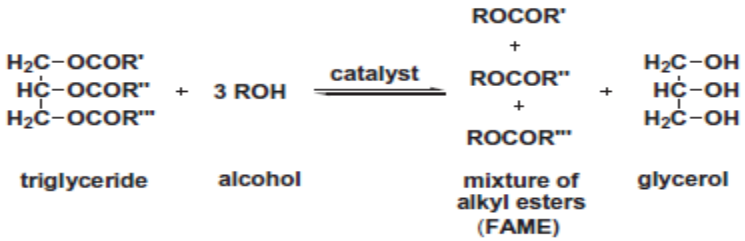
ABSTRACT

Increasing number of researches focusing on the use of solid heterogeneous catalysts for the production of biodiesel offers evidence that these catalysts continue to progress as viable alternatives. While alkaline metal alkoxides remain to be appealing in the industries, it is expected that solid base catalyst will soon become more attractive due to the financial and environmental concern. Limited investigations have shown that the conversion by solid base catalysts was analogous to that of the existing homogeneous system. This paper reviews various types of heterogeneous solid acids and bases in the production of biodiesel from transesterification of triglycerides. The conversion of vegetable oils from various catalytic systems are compared and discussed.

Keywords: Biodiesel, Transesterification, Heterogeneous catalysts, Solid base catalysts.

INTRODUCTION

Biofuels such as ethanol, biodiesel have been in focus for the reasons such as heavy consumption of fossil resources, effect on global warming and concerns of energy security. Biodiesel produced by transesterification of vegetable oils and animal fats using homogeneous base catalyst (Fig. 1) has seen several folds increase in last few years for their commercial production and use as a blending component in transport fuels.



R', R'', R''' = Hydrocarbon chain ranging from 15 to 21 carbon atoms

Fig. 1 Transesterification of vegetable oil

Conventionally, the biodiesel production is performed by transesterification of vegetable oils with methanol in the presence of homogeneous basic catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides. These catalytic systems suffer problems such as difficulty in removing the basic catalysts after the reaction, production of large amount of wastewater and emulsification. In this perspective, solid catalysts appear promising to replace the liquid homogeneous catalysts because they are less corrosive, easier to handle and separate, reusable and generating less amount of toxic wastes (Y. Feng and others, (2011)). The use of heterogeneous catalysis in transesterification reactions prevents the undesirable saponification, allows process simplification and offers reduction in the processing costs by eliminating the additional steps required by the liquid homogeneous catalysts.

BIODIESEL PRODUCTION FROM VEGETABLE OILS

Several oils, both edible and non-edible such as sunflower oil (Arzamendi and others, (2008)), palm (Li and Xie, (2006)) and jatropha (Tiwari and others, (2007)) have been transesterified for biodiesel production. In Europe and US, the primary sources for producing biodiesel are edible oils like rapeseed, sunflower, and soybean. In India, non-edible oils like jatropha and pongamia are being promoted on a very large scale, as these can be grown on marginal and waste lands (Azam and others, (2005)). Production costs have been reported to be rather high (Ma and Hanna, (1999)) as the process involves a number of washing and purification steps in order to meet the stipulated product quality. Oils with higher free fatty acid content lead to formation of soap and consequent loss of oil and problems of product separation (Kwiecien and others, 2009). Due to these issues a large number of alternative methods were developed. These include use of heterogeneous catalysts (Z. Helwani and others (2009)), supercritical process (Minami and Saka, (2006)) and enzymatic catalytic process (Shimada and others, (2002)). Biodiesel synthesis using heterogeneous solid catalysts instead of homogeneous liquid catalyst could potentially lead to economical production costs because of the possibility of reuse of the catalyst (Suppes and others, (2004)) both transesterification and esterification can be carried out simultaneously (Furuta and others, (2004)). Some researchers (Di Serio and others, (2008)) have reviewed the significance of solid catalysts for biodiesel production.

Heterogeneous catalysts reported, include ion-exchange resins, metal hydroxides, metal complexes (Abreu and others, (2003)), metal oxides such as calcium oxide (Granados and others, (2007)), magnesium oxide (Wang and Yang, (2007)), zirconium oxide (Jitputti and others, (2006)), zeolites, hydrotalcites and supported catalysts (Xie and Huang, (2006)). A comparison of properties of vegetable oils used for transesterification is presented in Table 1.

Table.1.Properties of vegetable oils

Vegetable oil	Kinematic viscosity at 38 ˚C(mm^2/s)	Cetane number (˚C)	Heating value (MJ/kg)	Cloud point (˚C)	Pour point (˚C)	Flash point (˚C)	Density (kg/l)
Corn	34.9	37.6	39.5	-1.1	-40.0	277	0.9095
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234	0.9148
Crambe	53.6	44.6	40.5	10.0	-12.2	274	0.9048
Linseed	27.2	34.6	39.7	1.7	-15.0	241	0.9236
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
Rapeseed	37.0	37.6	43.8	-3.9	-31.7	246	0.9115
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133
Soya bean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
Palm	39.6	42.0	–	31.0	–	267	0.9180
Babassu	30.3	38.0	–	20.0	–	150	0.9460
Diesel	3.06	50	39.3	–	-16	76	0.855

Heterogeneous catalytic transesterification: Different heterogeneous catalysts used for transesterification of various vegetable oils are listed in Table 2.

Table.2.Heterogeneous catalysts used for transesterification of vegetable oils

Veg. Oil	Catalysts	Alcohol	Amount of catalyst (wt. %)	Ratio OH/Oil	Time (h)	Temp. (˚C)	Speed (rpm)	Conversion (%)
Canola oil	Dolomite	Methanol	3	6:1	3	60	Const.	91.78
Cotton seed oil	Potassium fluoride loaded on alumina	Methanol	4	12:1	3	65	Const.	94
Palm oil	Novozym 435	Methanol	4	3:1	½	40	190	97
Rice bran oil	Dibutyl tin laurate	Methanol	1	4:1	4	60	Const.	68.9
Triacetin & Castor oil	12- Tungsto phosphoric acid	Methanol	0.00225 mole/dm^3	29:1	30	50-60	Const.	26
Palm kernel & crude coconut oil	(i) Zirconia (ii)Zinc oxide (iii)Sulphated zirconia (iv)zirconia supported potassium nitrate (v)Sulphated stannous oxide (vi)Zeolite supported potassium nitrate	Methanol	3	6:1	4	200	350	(i)69 (ii)98.9 (iii)96 (iv)78 (v)95.4 (vi)78
Rape seed oil	(i)Sodium hydroxide (ii)Mesoporous catalyst of Magnesium impregnated on Magnesium Nitrate (iii)Magnesium loaded on Aluminium hydrotalcite (iv)Potassium impregnated on Zirconia	Methanol	2	7:1	1	60	600	93 to 98
Soybean oil	Calcium oxide impregnated on lanthanum oxide, anion exchange resin	Mixtures of methanol and ethanol	8	10:1	½ 3	54	450	53 23
	N-methylimidazolium functionalized anion exchange resin	Methanol	2.5	12:1	10	50	570	97.35

CONCLUSIONS

This review suggests that the concern in heterogeneous catalysis for biodiesel production has been increasing. From the commercial point of view, solid base catalysts are seen more active than acid catalysts and enzymes. However, more researches on solid base catalysis are needed to validate this because the promising results from previously reported works were at the expense of high temperatures and high pressures. From the economic perspective, it would be ideal if solid base catalysts could work competently at low temperatures and pressure. However, these catalysts should continue to have a place in biodiesel synthesis so that more alternatives can be made available. Issues concerning their restrictions should also be addressed continuously so that the limitations can be overcome and they evolve as viable alternatives in the near future.

REFERENCES

Abreu, F. R., Melquizedeque B. Alves, Caio C.S. Macêdo, Luiz F. Zara and Paulo A.Z. Suarez (2005) New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterificaton reaction, Journal of Molecular Catalysis A: Chemical,227(1-2), 263-267.

Arzamendi, G., Arguinarena, E., Campo, I., Zabala, S., Gandia, L.M., (2008) Alkaline and alkaline-earth metals compounds as catalysts for the methonolysis of sunflower oil,Catal. Today, 133–135.

Azam, M.M., Waris, A., Nahar, N.M., (2005) Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India,Biomass Bioenergy,29, 293–302.

Di Serio. M, Riccardo Tesser, Lu Pengmei and ElioSantacesaria (2008) Heterogeneous Catalysts for Biodiesel Production, Energy Fuels, 22, 207–217.

Einloft. S, Tatiana O. Magalhães, Augusto Donato, JeaneDullius and RosaneLigabue (2008) Biodiesel from Rice Bran Oil: Transesterification by Tin Compounds, Energy Fuels, 22 (1), 671–674.

Feng.Y, A. Zhang, J. Li and B. He (2011) A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. Bioresource Technology, 102(3), 3607–3609.

Furuta. Satoshi, Hiromi Matsuhashi, and Kazushi Arat (2004) Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catalysis Communications, 5(12), 721-723.

Georgogianni. K.G., A.P. Katsoulidis, P.J. Pomonis and M.G. Kontominas (2009) Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts, Fuel Processing Technology, 90(5), 671-676.

Granados, M.L., Poves, M.D.Z., Alonso, D.M., Mariscal, R., Galisteo, F.C., Tost, R.M., et al., (2007) Biodiesel from sunflower oil by using activated calcium oxide, Appl. Catal. B: Environ.73, 317–326.

Helwani. Z., M R Othman, N Aziz, J Kim, W J N Fernando (2009) Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review, Applied Catalysis A: General , 363(1-2) , 1-10.

Ilgen.O. (2011)Dolomite as a heterogeneous catalyst for transesterification of canola oil. Fuel Processing Technology,92, 452–455.

Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., Jenvanitpanjakul, P., (2006) Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem. Eng. J. 116, 61–66.

Kim. M., C. DiMaggio , S. Yan , S.O. Salley , K.Y.S. Ng (2010) The synergistic effect of alcohol mixtures on transesterification of soybean oil using homogeneous and heterogeneous catalysts, Applied Catalysis A: General,378, 134–143.

Kwiecien, J., Hajek, M., Skopal, F., (2009) The effect of the acidity of rapeseed oil on its transesterification. Bioresour.Technol.100, 5555–5559.

Li, H., Xie, W., (2006) Transesterification of soybean oil to biodiesel with Zn/I2 catalyst. Catal.Lett.107(1), 25–30.

Lingfeng. C, Xiao Guomin, Xu Bo and TengGuangyuan (2007) Transesterification of Cottonseed Oil to Biodiesel by Using Heterogeneous Solid Basic Catalysts, Energy Fuels, 21 (6), 3740–3743.

Long.T., Y. Deng, G. Li, S. Gan and J. Chen (2011) Application of N-methylimidizolium functionalized anion exchange resin containing NaOH for production of biodiesel. Fuel Processing Technology, 92 (7), 1328-1332.

Ma, F., Hanna, M.A., (1999) Biodiesel production: a review.Bioresour.Technol. 70, 1– 15.

Minami, E., Saka, S., (2006) Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process. Fuel, 85, 2479– 2483.

RahmanTalukder. M. M., J. C. Wu, S. K. Lau, L. C. Cui, G. Shimin and A. Lim (2008) Comparison of Novozym 435 and Amberlyst 15 as Heterogeneous Catalyst for Production of Biodiesel from Palm Fatty Acid Distillate, Energy Fuels, 23 (1), 1–4.

Rubio .A. C. A., Jose´ Santamarı´a-Gonza´ lez , Josefa M. Me´ rida-Robles , Ramo´n Moreno-Tost ,David Martı´n-Alonsob, Antonio Jime´nez-Lo´ pez , Pedro Maireles-Torres (2010) Heterogeneous transesterification processes by using CaO supported on zinc oxide as basic catalysts, Catalysis Today,149, 281–287.

Shimada, Y., Watanabe, Y., Sugihara, A., Tominaga, Y., (2002) Enzymaticalcoholysis for biodiesel fuel production and application of the reaction to oil processing. J. Mol. Catal. B: Enzym,.17, 133–142.

Suppes, G.J., Dasari, M.A., Doskocil, E.J., Mankidy, P.J., Goff, M.J., (2004) Transesterification of soybean oil with zeolite and metal catalysts. Appl. Catal. A: Gen. 257, 213–223.

Tiwari, A.K., Kumar, A., Raheman, H., (2007) Biodiesel production from jatropha oil (jatrophacurcas) with high free fatty acids: an optimized process. Biomass Bioenergy 31, 569–575.

Wang, L., Yang, J., (2007). Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol.Fuel,86, 328–333.