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Transesterification of Virgin and Waste Oil by TiO_2/KI as an Effective Heterogeneous Catalyst

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Abstract : TiO_2 impregnated KI was used as a heterogeneous catalyst in different concentrations (3wt%, 5wt% and 10wt%) for the transesterification of various virgin and waste cooking oils. Transesterification reaction parameters were varied to obtain the maximum yield of biodiesel. In the course of study it was observed that the maximum conversation of virgin/waste oil to the biodiesel was observed in the 10wt% amount of catalyst when tried with the various reaction timings. The biodiesel can be separated by the usual methods and the catalyst left over after separation can be reused for 5 times without effecting much on the conversions. The optimum reaction condition obtained or achieving maximum conversion >97% were – 6:1 methanol to oil molar ratio, 5 h of reaction time, 10 wt% catalyst amount (reusability 5 times) and 65 °C reaction tim.
Key words: Transesterification, Heterogeneous Catalyst, Biodiesel, Waste oi.

Introduction

The demand in the world for petroleum-based fuel is increasing with the population explosion, these sources are limited and definitely not environmental friendly. Hence there is a need for the alternate sources of the fossil fuels and is a concern for the recent researchers[1-7]. One of the possibility we are eyeing on is the simple transesterification of virgin and waste vegetable oils with methanol resulting in fatty acids of methyl ester commonly known as biodiesel. There is a potential in it to reach the need of humans in this era as it is renewable sources of energy with plenty of options available, environmental friendly as well. Our goal is to make it economical and available for commercial uses. This fuel has been found to have better quality in terms of cetane number, flash and fire points, lubricity and other like characteristics without compromising with the heat of combustion[8-14].The commercial biodiesel can be produced by the simple transesterification reaction in alcohol, forming fatty acid esters to methyl esters i.e. displacing an alcohol from the parent oil compounds. This reaction is very slow hence to accelerate the rate of reaction we look for different catalyst options. As shown in fig.1 the reaction is a reversible, the role of the catalyst is to increase the rate of reaction in the forward direction.

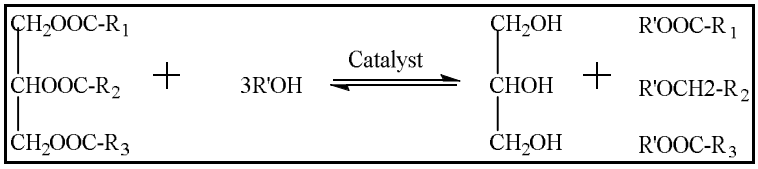

Fig. 1. Transesterification of Triglycerides rom Oils

If we look at the stoichiometry of the reaction 3:1 methanol to oil ratio is needed, but practically higher ratio is used to accelerate the reaction in the forward direction[15]. Catalyst used here can be homogenous, as it is an easy method for transesterification but since the workup processes are tedious as it involves lots of complex separation techniques, various purification techniques due to homogenous nature of the reaction mass. Moreover there is a tendency of formation of emulsion[16]during this process which adds more complexity in the separation of biodiesel. All these drawbacks are added to the cost of the produced biodiesel hence making in inconvenient for the practical large scale industrial and commercial applications. Hence heterogenous transesterification is the choice of the researchers these days as moderate conditions are required and reusability characteristics reduces the extra impact on the environment[17,18].Metal oxides has been the first choice for the researchers currently for the conversion, as various metal oxides and mix metal oxides including and not limited to alkaline earth metal oxides, Mg-Zn mix metal oxides, calcium based metal oxides derived from various sources and different combination of Zn, Mg, Al, Fe metal oxide[19-23]. To increase the basic strength of metal oxide doping has been introduced in the recent past. As potassium ions contributing to the highest basicity when added to metal oxides resulting in to base catalyst with higher conversion of oils to biodiesel with simple reaction conditions and lesser conversion time. Potassium salts like KOH, KI, KBr, KCl and KF have been studied by till the date and have been found effective[24-28]. Here in we report transesterification by the TiO_2/KI in a heterogeneous conditions with 5 times reusability of the catalyst.

Experimental:

Materials and Methods

All the chemicals used were of analytical grade. The virgin and waste sunflower oil, coconut oil, cotton seed oil, castor oil were purchased from local shops located in Phagwara, India. The FTIR studies were done onShimadzu FT-IR-8400 instrument, the^{1}HNMR studies were performed on Bruker (Avance III), 400MHz instrument using $CDCl_3$ as a solvent and TMS as internal standard.

Preparation of the catalyst

KI impregnated TiO_2 catalyst was prepared by wet impregnation method. TiO_2 was impregnated with 50% of KI. In the preparatory method, 4 g of analytical grade TiO_2 was taken in 40 ml of petroleum ether and 2 g of KI crystals was subsequently added to it grinded in the mortar pastel for 3 hours at room temperature. The mixture was left to the room temperature until it got totally dry. The dried powered was pressed in the KBr pressure machine and thus formed pellets were calcinated in the muffle furnace at 800°C for five hours. The resulting catalyst was used for all the reactions.

Trans-esterification

The reaction was carried out at 65 °C using 6:1 methanol to oil ratio for 5 h. Using 3 wt%, 5 wt% and 10 wt% catalyst (TiO_2/KI). After completion of the reaction the catalyst was separated from the reaction mass and washed with the methanol followed by petroleum ether thrice and was reused for 5 times without effecting much on the yield. After completion of the trans-esterification reaction, the reaction mixture was kept in a separating funnel and glycerol was allowed to settle at the bottom of the funnel and was removed from mixture. From the biodiesel layer methanol was evaporated under vacuum and residue was taken for characterization by FT-IR and ^{1}H NMR.

Result and Discussion

Various chemical parameters are necessary to determine before using the oils for the purpose of making biodiesel. Hence the FFA, saponification, and moisture content of the sample oils were determined by literature-reported methods[29] and the results are shown in Table 1.

Table 1 . Chemical Analysis of Vegetable Oils*

Sr.No	Name of the Oil	FFA value (wt %)	Moisture content (wt %)	Saponification value (mg of KOH/g)
1	Sunflower oil	1.4	0.3	122.12
2	W. sunflower oil	2.3	0.4	123.01
3	Coconut oil	0.8	0.5	102.56
4	W. Coconut oil	1.1	0.4	103.21
5	Cotton seed oil	0.2	0.3	101.84
6	W. cotton seed oil	1.8	0.4	102.27
7	Castor oil	1.9	0.6	97.25
8	W. castor oil	3.5	0.5	98.85

*W. = waste

In recent past the metal oxide catalyst have made a remarkable impact on the synthesis of biodiesel in both nano and macro physical state e.g. MgO, CaO, $Ca(C_2H3O_2)_2$/SBA-15, $Ca(OCH_3)_2$, SrO, Fe_2O_3, CuO, Fe_3O_4, ZnO/$Sr(NO_3)_2$, Li/MgO, Li/Mg(Al)O CaO–ZnO and CaO–La_2O_3. Metal oxide impregnated catalyst like ZnO/KF, Al_2O_3/KI, ZnO/I_2, have also caught attraction among the researchers[30-36]. Our method is also an improvement of the reported process which is good at lower reaction conditions and reusability of the catalyst.

The amount of catalyst used and timing were varied as the reaction was performed with various amountof the catalyst with the reaction time 1 to 7 hr. The yield started increasing as the reaction time was increased but after 5hr the yield started decreasing a little hence we have chosen the reaction timing as 5 hr in all the cases. The amount of catalyst plays a major role for any chemical reaction, herein we have tried 3%wt to 10%wt weight of catalyst as shown in Table 2. We have found maximum yield formation in the various oils with 10%wt concentration further increase in the amount of catalyst didn't affect the yield much.

Table 2 : Optimization of Catalyst Amount*

Sr. No	Name of the Oil	Catalyst amount	Yield%	Catalyst amount	Yield%	Catalyst amount	Yield%
1	Sunflower oil	3% wt	69.12	5% wt	86.02	10% wt	94.28
2	W. Sunflower oil	3% wt	68.10	5% wt	85.26	10% wt	94.52
3	Coconut oil	3% wt	56.92	5% wt	88.24	10% wt	**97.72**
4	W. Coconut oil	3% wt	60.26	5% wt	89.21	10% wt	95.23
5	Cotton seed oil	3% wt	64.20	5% wt	86.20	10% wt	93.63
6	W. Cotton seed oil	3% wt	61.29	5% wt	88.21	10% wt	92.23
7	Castor oil	3% wt	63.95	5% wt	83.15	10% wt	94.63
8	W. castor oil	3% wt	65.18	5% wt	85.23	10% wt	93.21

*W. = waste

The IR spectrum for various oil showed the ester linkage of the fatty acid methyl ester at in the range of 1736-1743 cm^{-1}. NMR analysis in $CDCl_3$ using TMS as internal standard. The conversion of the various oil to a mixture of the methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of the methyl esters) and 2.30 ppm (a-carbon CH_2 groups of all fatty acid derivatives) according to the reference. Which confirms the formation of the fatty acid methyl ester also known as biodiesel[37-38].

Reusability Study:

The reusability of the heterogeneous catalyst is an important advantage over the homogeneous catalyst because the same could reduce the overall processing cost of a chemical reaction. To test the reusability of TiO_2/KI, transesterification of the oils were performed with methanol under optimized reaction conditions. After the completion of the reaction, TiO_2/KI was recovered from the reaction mixture by filtration, washed with petroleum ether, and calcinated at 800°C. The catalyst hence recovered and regenerated was employed for 5 successive catalytic cycles under the same experimental and regeneration methods.

Conclusion

TiO_2/KI has potential application as a renewable resource of catalyst for biodiesel production. The catalyst was obtained by calcinations of TiO_2 with 50% KI at 800 °C for 5 h. The maximum yield of biodiesel produced by transesterification of coconut oil with methanol was 97.72%. The operating condition to achieve the maximum biodiesel yield is: the ratio of oil to methanol 1:6, the amount of catalyst 10 wt%, reaction time 5 h, reaction temperature 65 °C. Current study is going on for large scale preparation of biodiesel and applications of the same in the engines.

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