Heterogeneous Catalysis of Yemeni Jatropha oil over MgO/TiO$_2$ Catalyst

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ABSTRACT─ *Jatropha as an non edible plant is a promising plant for biodiesel production Positive environmental impacts from the cultivation of this plant including the improvement of wasteland, sustainable employment for local people, and carbon farming. For industrial biodiesel production, homogeneous basic catalyst, including KOH, NaOH, as well as potassium and sodium alkoxides, are commonly used for the transetrification of Jatropha oils with methanol to produce fatty acid methyl ester. However the base-catalyzed process suffers from several drawbacks, such as difficulty in recycling catalyst and environmental pollution. The aim of this paper is to circumvent homogeneous process problems, attempts to use heterogeneous catalysts in the transetrification of Jatropha oils.*

Titanium supported MgO catalyst samples (10 and 20 wt % MgO loading) were prepared by incipient wetness impregnation method and characterized using FTIR, XRF, BET and XRD techniques. These materials were tested as catalyst for the conversion of Jatropha oil to biodiesel in the presence of methanol. The effects of reaction temperature, reaction time and MgO loading on the Jatropha oil conversion have been established.

It was observed that for the same reaction time and MgO loading, increasing the reaction temperature increased the biodiesel yield. For example, the oil conversion over 20% MgO/TiO$_2$ catalyst after 60 min of reaction at 60°C, 150°C, 175°C, 200°C and 225°C was found to be 42,55,86,89 and 100% respectively. An increase in oil conversion was also observed when the reaction time was increased. For example, biodiesel yield of 37, 43, 50, 51, for 10% MgO/TiO$_2$ after 15, 30, 45 and 60 min respectively were measured at 175°C.

Catalytic properties for MgO/TiO$_2$ solid catalyst were evaluated for the conversion of Jatropha oil to biodiesel. The effects of reaction temperature, reaction time and MgO loading on the Jatropha oil conversion have been established. It was observed that oil conversion increases with the increase in reaction temperature and reaction time. The effect of MgO loading on the Jatropha conversion was found to depend on the operating temperature. An increase in Jatropha oil conversion with an increase in MgO loading was observed at reaction temperature above 150°C, So the cultivation of Jatropha in Yemen will improve the economic and environmental situation. In addition the researches should be continued for getting more reused catalyst with sufficient properties.

Keywords— heterogeneous, transetrification, Jatropha

1. INTRODUCTION

The potential benefits of the spread of Biodiesel Crops to society are far more than just reducing environmental damage. Through adopting technologies that reduce energy, water and resource usage, societies will increase their productivity, their global competitiveness and drive local economic development and employment. The ultimate goal of Bio-energy is to integrate it into everything we do, and, in the words of Vinod Khosla (one of the world's leading green energy venture investors), to become 'maintech (Jain et al 2009, Lang et al 2001) . The category will then not be something special: it will just be the way things are done.

Clean Technology investment is therefore not just about providing the scientific foundation for future technologies. Green energy is an essential part of the transition to a world in which efficiency improve, productivity and economic growth improves, and communities function more effectively.

2. SUSTAINABILITY

Given the realities of the biodiesel markets, a successful biodiesel business plan begins with an effective feedstock strategy from which process design flows. To make biodiesel a long-term business opportunity, attention must be given to the critical issue of availability of right feedstock at right cost. Jatropha and other nonfood feed stocks will be a vast

source of biofuel and a key to reducing our dependence on fossil fuel Jatropha can bring significant environmental benefours. It can replace jet fuel and diesel from petroleum without interfering with food crops or leading to the clearing of forests. The good thing about Jatropha is that you're producing a tree shrub that lives for a long time and does ours job, producing oil, while it also sequesters lots of carbon dioxide from the atmosphere .

Jatropha is a valuable multi-purpose crop that can help to alleviate soil degradation, desertification and deforestation, and it can be used for bio-energy to replace petro-diesel, for soap production and climatic protection, and hence deserves specific attention. Jatropha can help to increase rural incomes, self-sustainability and alleviate poverty for women, elderly, children and men, tribal communities, small farmers. It can as well help to increase income from plantations and agro-industries (Kazi et al 2006, Le Tu Thanh et al 2012, Teresa et al 2016).

Benefits to Developing countries in general and Yemen in particular:

- Wasteland Reclamation and Reforestation

- Income generation from previously unusable areas

- Provide huge opportunities from new sustainable and renewable land resources

- Crops Creating employment Nursery development, soil preparation, irrigation systems, Plantation maintenance, seed collection, oil extraction and Refinery control

- Benefit from the increased demand for employment in infrastructure, logistics and Transportation

For industrial biodiesel production, homogeneous basic catalysts, including potassium hydroxide, sodium hydroxide, as well as potassium and sodium alkoxides, are commonly used, but the process suffers from several drawbacks, such as difficulty in recycling catalyst and environmental pollution. **(**Kamila Colombo et al 2017).

To circumvent homogeneous process problems attempts to use heterogeneous catalysts in the transetrification of Yemeni Jatropha oils have been made.

These catalysts can be easily separated at the end of reaction and may also be reused (Xie et. al 2009, Gui et al 2008, Pati et al 2009) .

3.   Aim of the study

This study aims at evaluating catalytic activities for MgO/TiO2 as a heterogeneous catalytic system on the conversion of Yemeni Jatropha oils to biodiesel in presence of methanol. The effects of reaction parameters such reaction time, reaction temperature and catalyst loading on the overall Jatropha oil conversion to biodiesel has been evaluated.

4.   Experimental Details

4.1 Catalyst Preparation

Support preparation:

TiO2 powder was mixed with distilled water in a 1:1 weight ratio and dried at 120° C overnight. The sample was thereafter calcined in air at 500° C for 10 h and crushed and sieved to retain particles with sizes between 50 and 150 μm for use as catalyst support.

MgO loading:

An appropriate amount of an aqueous solution of Mg (NO3)2 .6 H2O (Sigma Aldrich was added to the TiO2 support which was subsequently dried at 120° C followed by calcinations in air at 500° C for 8 h to decompose the nitrate to MgO in the catalyst. Catalyst samples with 10 and 20 wt.% MgO loading were synthesized

4.2 Catalyst Characterization

The MgO loading in catalyst samples was determined by XRF analysis on a MAGIX PRO XRF spectrometer. The structure of the catalyst was determined by X- ray diffraction (XRD) analysis on a Philips PW 3040/60 apparatus with a CuK α (λ = 0.154 nm) radiation over a 2θ range of 4 – 130 ° (with a 0.02 ° step size and a scan speed of 0.04 s/step . BET analysis was performed on Micro meritics ASAP 2000 apparatus to determine the surface area and pore size distribution by N2 adsorption at a temperature of 77 K. Functional groups in the catalyst samples were determined by

Fourier Transform Intra- Red (FTIR) analysis using a Bruker Tensor 27 with a pike Golden Gate ATR attachment in the range of 4000- 400 cm -1

4.3 Determination of acid value for Jatropha oil

The acid value (A.V) was determined according to the standard method II.D.1 adopted by the IUPAC [79]. The method is based on titrating the free fatty acids present in oil using ethanolic KOH solution and phenolphthalein as indicator. The oil sample was dissolved in a 1:1-solvent mixture of 96% ethanol and diethyl ether. The acid value is given as the number of mg of KOH needed to neutralize 1g of Oil and can be calculated according to equation (1):

$$A.V = \frac{56.11 \times T \times V}{m} \dots \qquad (1)$$

Where 56.11 is the molecular weight of KOH, T is the exact normality of standardized KOH solution, V is the volume of KOH solution needed to reach the end point of titration and m is the mass of oil in gram.

4.4 Catalyst Testing

Catalyst testing was carried out in a stainless steel stirred batch reactor (PARR 4842seriesreactor, 300 cm3) loaded with Jatropha oil (68 cm3, acid value: 11.1mg of KOH/g, moisture: 0.12 wt.% ,methanol (52 cm3) and varying amounts of catalyst. The reaction was carried out at 60, 100 , 150, 200 and 225 ° C respectively. A small sample was collected from the reactor after every 15 min and left to cool to room temperature. The product was then heated at 65° C in a vacuum evaporator to remove any methanol. The products that remained separated into two phases: glycerol as the bottom phase and unreacted Jatropha oil and formed methyl ester (biodiesel) as the top phase. The latter was used to determine the oil conversion to methyl esters using NMR data and the following equation (2) (Knothe, 2001) :

$$\% \text{ Conversion} = \frac{2 \text{ AME}}{3 \text{ A } \alpha - CH2} \qquad (2)$$

Where AME is the integration value of the protons of the methyl esters;
A α – CH2 is the integration value of the methylene protons.

5. RESULTS AND DISCUSSION

5.1 Catalyst characterization

Fig. 1 shows the FTIR for the dried catalyst (spectrum a and the calcined20% MgO- TiO2 (spectrum b). It was reported in literature that the peaks at 1620 – 1640 and 3100 – 3500 cm -1 can be attributed to the O- H bending vibration mode and O- H stretching vibration mode of the adsorbed water molecules respectively and the absorbance between 400 and 1000 cm -1 original from titanium dioxide can be assigned to the O – Ti – O lattice vibration (Mi-na et al 2011).

As supported by literature, O – H bonds of water molecules present in the dried sample were observed at 3353 cm –I and 3247 cm -1. At 1646 cm -1

O-H bonds were also observed due to bending of molecular water, NO_3 - which is predominant in the dried sample was observed at 1346 cm -1and Mg (OH)$_2$ was observed at 819 cm -1. The water transmittance peaks were not observed on the calcined catalyst sample suggesting that all the moisture was removed after calcinations at 500°C. Also no NO_3 - transmittance peak as observed in the calcined sample suggesting complete decomposition of Mg (NO_3)$_2$ during the calcinations process.

Fig. 2 shows the XRD patterns of dried catalyst sample (pattern a) and calcined 20% MgO/ TiO2 catalyst sample (pattern b). The XRD pattern for the calcined 20% MgO/ TiO2 has three additional diffraction peaks detected at ca. 37.0, 43.2 and 78° compared to the calcined blank support. Theses peaks were attributed MgO , in agreement with (Corma et al. 2000) who reported XRD diffraction peaks for MgO at 20 = 37° , 42.9° , 64° , 67° and 78°.

Using the XRD data, the crystallite sizes of MgO in 10% MgO/ TiO2 and 20% MgO/ TiO2 were calculated and found to be 17.4 and21.3 nm respectively.
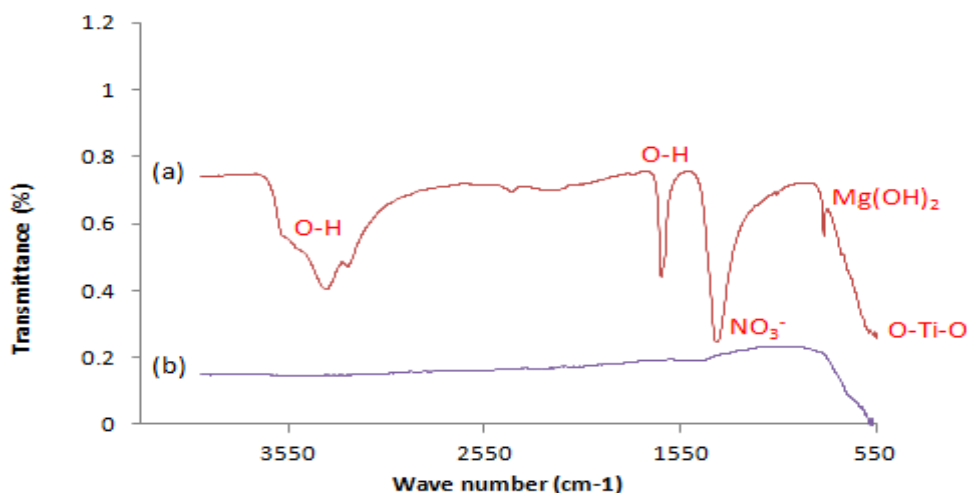
Figure 1: FTIR spectrum of (**a**) dried catalyst; (**b**) 20% calcined MgO – TiO2
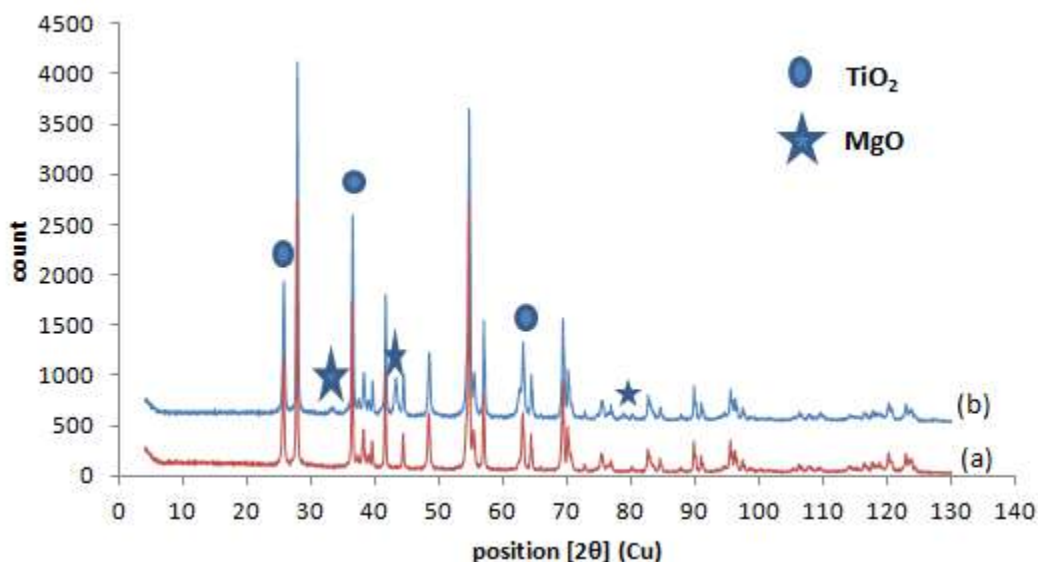

Figure 2: XRD pattern of (**a**) calcined blank TiO2; (**b**) 20% MgO- TiO2

Fig.3. below shows the XRD pattern of the calcined 20% MgO/ TiO2 before and after reaction at 150° C and 225 ° C for 1 h. before the catalyst gets involved in the reaction, the intensity of the peaks is the same after reaction suggesting that the catalyst structure was not altered during reaction. The crystallite sizes of MgO in 10% and 20% MgO/ TiO_2 were re- calculated after the catalyst was involved in the transetrification reaction at 225° C and were found to be17.01 and 21.02 nm respectively. These sizes are almost the same as before the reaction and suggest that no sintering of the catalyst happened during the reaction.

The XRF analysis results for MgO/ TiO2 are summarized in table 1 below:

Table 1: XRF Analysis Results For The Prepared Catalysts

Target % MgO	Obtained % MgO
10	10.2
20	20.4
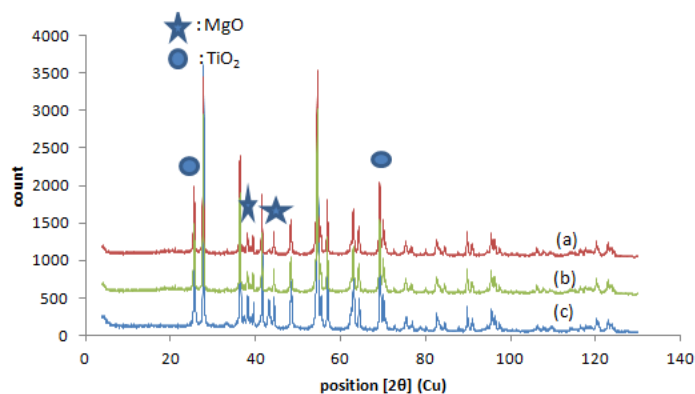
Figure 3: XRD pattern of calcined MgO/ TiO2 catalyst **(a)** before reaction; **(b)** after the transetrification reaction at 225 °C for 1 h

The measured MgO loading was satisfactorily closer to the target loading for all the samples. The surface area and pore size diameter for the calcined blank TiO_2 support, and calcined 10% MgO/TiO_2 and 20 % MgO/TiO_2 are summarized in table 2 below:

Table 2: Summary of BET DATA

	Calcined blank TiO$_2$	**10% MgO/TiO$_2$**	**20% MgO/TiO$_2$**
Surface area (m2/g)	21.7	13.1	14.9
Pore size (nm)	47.4	44.4	45.3

Calcined blank TiO2 had a surface are of 21.7 m2 /g and a pore size of 47.4 nm. The surface area and pore size decreased at 10% MgO loading to 13.1 m2/g and 44.4 nm respectively. For 20% MgO loading the surface area decreased to 14.9 m2/g while the pore size was 45.3 nm. The decrease in surface area and the pore size with the increase in MgO loading can suggest some degree of pore obstruction in the TiO2 support by MgO.

5.2 Catalyst Testing

Fig.4 and5 show the Jatropha oil conversion to biodiesel as a function of reaction temperature, time and MgO loading on the TiO_2 support.

It was observed that for the same reaction time and MgO loading, increasing the reaction temperature increased the biodiesel yield. For example, the oil conversion over 20% MgO/ TiO$_2$ catalyst after 60 min of reaction at 60° C (Fig. 4a), 150° C (Fig. 4b), 175° C (Fig4c), 200° C (Fig 4d) and 225° C (Fig. 5a) was found to be ca. 42, 55, 86, 89 and 100% respectively.

The increase in oil conversion with the reaction temperature increase can be explained by the fact at high temperatures, the oil solubility in methanol increases leading to lower resistance to mass transfer. The viscosity of the oil also decreases and promotes better mixing between reactants and catalysts (Gan et al 2010) . An increase in oil conversion was also observed when the reaction time was increased. For example, biodiesel yield of ca. 37, 43, 50, 51 for 10% MgO/ TiO$_2$ after 15, 30, 45 and 60 min respectively were measured at 175° C (Fig. 4c) . these data(Fig. 4 and 5) also show that under same operating are measured on the catalyst with the highest MgO loading (20% % MgO/ TiO$_2$). When compared at a short reaction time, the effect of MgO loading on the oil conversion was found to be less significant for reactions performed at 60 and 150° C (Fig 4a and b respectively) where the relative difference in oil conversion measured on 10 and 20% MgO loaded catalysts is less than 10%

This effect becomes more significant for the reaction performed at 175° C (Fig 4c) where the oil conversion measured on the 20% MgO/ TiO$_2$) catalyst was approximately double of the 10% MgO/ TiO$_2$ catalyst. An increase in reaction temperature to 200 ° C (Fig 4d) resulted in the decrease of the effect of MgO loading on oil conversion as compared to the reaction at 175° C and almost no MgO loading effect was measured on the performed at 225° C (Fig. 5).

In order to understand the dependence of the MgO loading effect on the reaction temperature, additional reactions with no catalyst and with the blank TiO$_2$ support were respectively performed at 225° C. The data are also reported in Fig.5 and show that ca. 5 and 22% oil conversions were reached after 15 min of the uncatalysed reaction and of the reaction over the blank TiO$_2$ respectively. All the data combined suggest the following:

1) At reaction temperatures of 60 and 150° C , the reaction is more mass transfer- controlled and explains the less significant effect of MgO loading effect on the oil conversion .

2) The mass transfer seems to improve at temperature above 150 ° C causing more reacting species to access the active sites in the catalyst. In this case the reaction is more controlled by the active sites density in the catalyst. This can explain the high oil conversion measured in the reaction performed at 175°C on the 20% MgO/ TiO$_2$ catalyst that has more MgO active sites than the10% MgO/ TiO$_2$.

3) As the reaction temperature is increased above 175° C, the contribution from the TiO$_2$ support to the oil conversion becomes more significant and makes it difficult to establish the net effect of the MgO loading on the reaction.
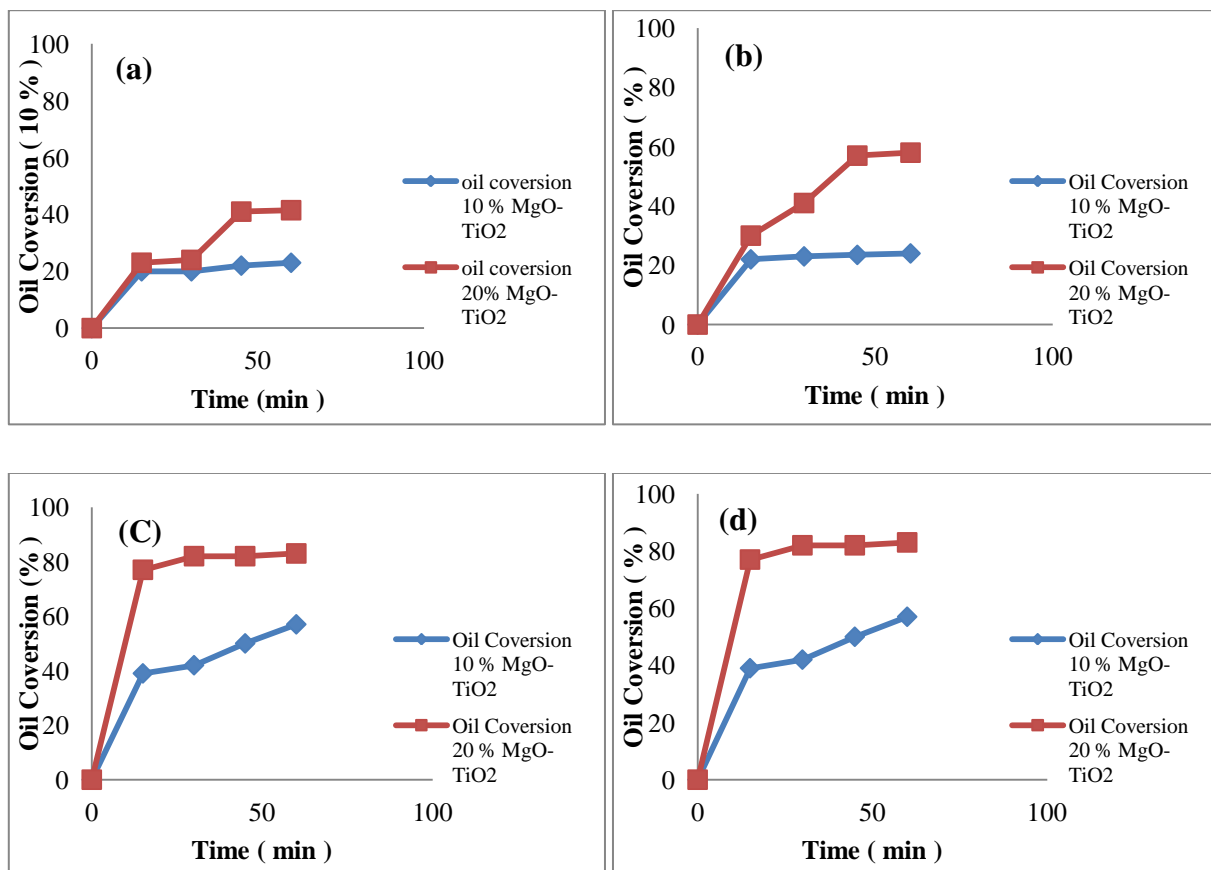
Figure 4: effect of time and MgO loading on Jatropha oil transetrification at **a)** 60° C; **b)** 150°C; **c)** 175° C and **d)** 200° C (alcohol to oil molar ratio 18: 1, catalyst amount 3wt.% MgO/TiO$_2$)
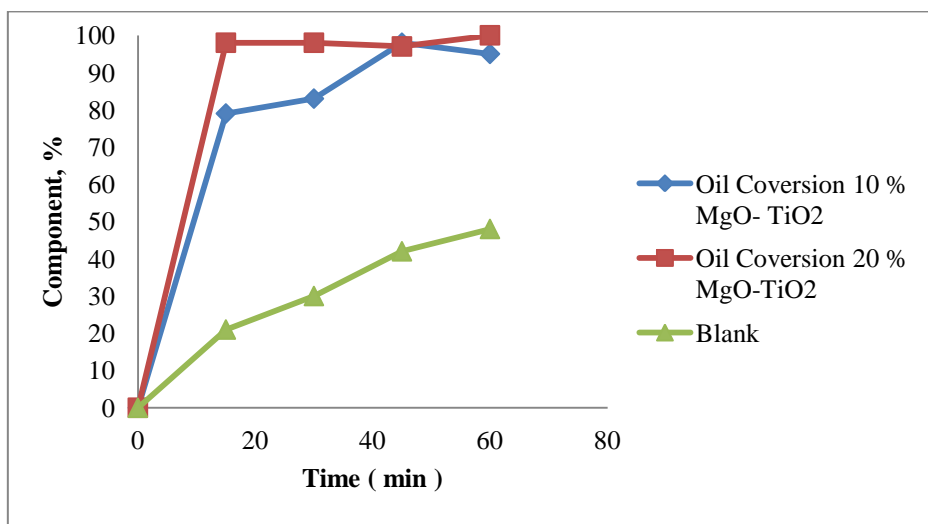
Figure 5: Jatropha oil conversion to biodiesel as function of time respectively over blank TiO_2 and over 10 and 20% MgO/TiO_2 catalyst (alcohol to oil molar ratio 18:1, catalyst amount 3 wt.%, 225° C

6. CONCLUSION

Catalyst properties for Mg/TiO_2 solid catalyst were evaluated for the conversion of Jatropha oil to biodiesel. The effects of reaction temperature, reaction time and MgO loading on the Jatropha oil conversion have been established. It has been observed that the oil conversion increases with the increase in reaction temperature and reaction time. The effect of MgO loading on the Jatropha oil conversion was found to depend on the operating temperature. less significant effect of MgO loading was observed at temperature up to 150° C after 15 min of reaction possibly because the reaction was more mass transfer – controlled. An increase in Jatropha oil conversion with an increase in MgO loading was observed at reaction temperatures above 150° C but it was difficult to establish the net effect of MgO loading for the reactions performed at temperatures above 175°C because of the contribution from the TiO_2 support to the oil conversion.

7. ACKNOWLEDGMENT

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