



AN EFFICIENT ROUTE TO GAS PHASE SYNTHESIS OF HIGH PURITY 1-DECENE OVER γ -ALUMINA

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Abstract

The aim of this research is to optimize the formation of 1-decene. Conversion of 1-decanol to 1-decene, di-*n*-decyl ether and internal olefins using γ -Al₂O₃ as the catalyst was investigated in a fixed-bed reactor varying the temperature between 300-340 °C and flow rate between 0.2-0.14 mL/min. The influence of using nitrogen as the carrier gas was also observed. Results have shown that an increase in temperature will favor the formation of olefin and reduced the formation of di-*n*-decyl ether. The conversion increases gradually from 90% at 300 °C to 100% at 350 °C. However, an increase in temperature also promotes the formation of internal olefins which are impurities in the product. When nitrogen gas is used as carrier gas there is very trace formation of di-*n*-decyl ether at high flow rate of 1-decanol. The optimized flow rate of 1-decanol is 0.10 mL/min using 2.0 g of γ -Al₂O₃.

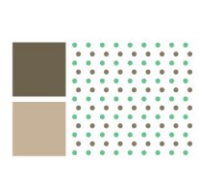
Keywords: dehydration reaction, γ -Al₂O₃, double bond migration, internal olefin, 1-decene

Introduction

Transportation has played a prominent role in the economic growth of ASEAN countries. In order for the ASEAN economic cooperation to maintain its comparative advantage, the component of transportation cost, such as the price of fossil fuel and lubricating oil from crude oil needs to be controlled. Unfortunately, since we are running short of petroleum reservoir, an increase in price of petroleum-based products is inevitable. The time has come to look for alternative sources of raw material to replace declining crude oil. So far there has been a lot of research on conversion of natural oil to bio-diesel (Schuchardt et al., 2006). However, very little work has been done on lubricating oil, despite the fact that the demand for lubricating oil also increases with the demand for diesel oil (Mortier et al., 1998).

For more than a decade, synthetic lubricant or Polyalpha-olefin (PAO) has been known for its high viscosity index (thermal stability) and high oxidation stability (Fatourehchia et al., 2011). Presently commercial synthetic lubricant is produced from 1-decene which is obtained primarily by processing crude oil. Fortunately, we have realized that natural oil can also be used to produce 1-decene. However, natural oil will have to be transformed to 1-decanol first. Then 1-decanol can be converted to 1-decene through the dehydration reaction.

The dehydration reaction is usually catalyzed by heterogeneous acid catalyst such as SAPO-34 (Fatourehchia et al., 2011), sulfated zirconia/ γ -Al₂O₃ (Skrdla, 2003), HZSM-5 (Ivanova et al., 2009), Ti/ γ -Al₂O₃ (Skrdla et al., 2003), WO₃/ZrO₂ (Baertsch et al., 2002), mesoporous boron-alumina (Xiu et al., 2011) and mesoporous γ -Al₂O₃ (Sung et al., 2012). So far it can be stated that the most active catalyst for dehydration reaction is γ -Al₂O₃. Various studies have already been reported on the dehydration of small molecular weight alcohol, such as



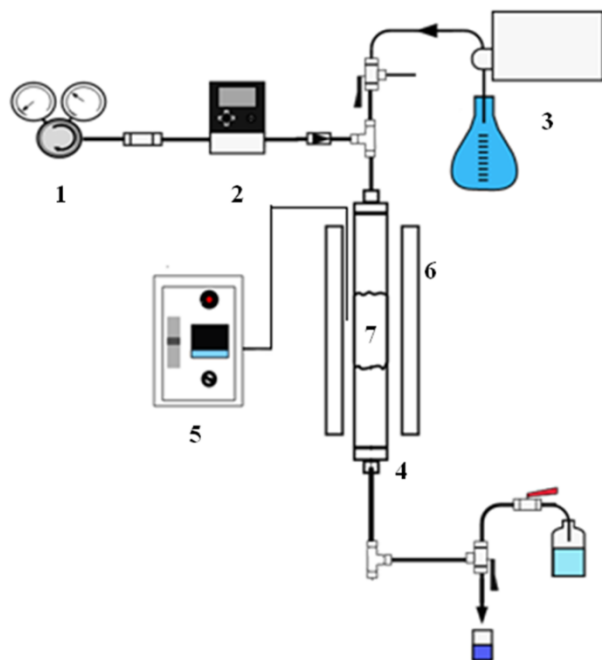
methanol (Najafabadi et al., 2012), ethanol (Kagymanova et al., 2011), butanol (West et al., 2009) and 1-phenylethanol (Bertero and Apesteguia, 2009). Recently, results from dehydration of larger molecular weight alcohol showed that yield of olefin is greater at higher temperature. On the other hand, formation of ether will be favored at lower temperature. Mark A. Keane et al. first reported the used of Ni metal on sodium zeolite Y, obtained by means of ion exchanging of Ni^{3+} with NaY, in the dehydration of 1-hexanol. Although activity is increased when Ni is used, there is still an obvious sign of catalyst deactivation (Park and Keane, 2001). Meanwhile, the conversion of 1-octanol, 1-nonanol, 1-decanol and 1-dodecanol over $\eta\text{-Al}_2\text{O}_3$ catalyst at 350°C and reactant flow rate of 0.026 mol h^{-1} was roughly 97%, 93%, 55% and 87% (Nel and Klerk, 2009). Another important parameter that has not been observed sufficiently is the effect of the flow of inert nitrogen gas on the conversion and selectivity of the dehydration reaction. Additionally, there has been little knowledge of the dehydration reaction of larger fatty alcohol such as 1-decenol.

In this work we aimed to investigate the conversion of 1-decanol, obtained from natural oil and fats, to 1-decene which can be used as the feedstock for production of synthetic lubricant oil in the future. An optimum operating condition is found by varying the temperature between $300\text{-}350^\circ\text{C}$, weight hourly space velocity (WHSV) between $0.5\text{-}4 \text{ h}^{-1}$ and flow rate of inert gas between $0\text{-}150 \text{ mL/min}$. Our results will provide quantitative substantial references used to pioneer the production of 1-decene from 1-decanol at an industrial level.

Methodology

A commercial alumina $\gamma\text{-Al}_2\text{O}_3$ (Aluminum sphere obtained from Sasol Company, with surface area $205 \text{ m}^2/\text{g}$ and pore volume of $0.75 \text{ cm}^3/\text{g}$) was used as an acid solid catalyst for the dehydration reaction in a stainless fixed-bed reactor of 15 mm internal diameter. Approximately 1.0-2.0 grams of catalyst loaded in the middle of the reactor with ceramic balls on the top and bottom of the catalyst bed. The ceramic balls were used to pre-heat the feedstock at the top of the reactor and to support the catalyst bed so that it remains in the center throughout the experiment. Layers of glass wool were used to separate each layer inside the reactor. All experiments are performed at atmospheric pressure.

After loading the reactor with ceramic balls and the catalyst, the reactor was purged with 150 mL/min of nitrogen gas flow at the reaction temperature for 2 hours. A HPLC pump is then employed to deliver a specific flow rate of 1-decanol into the system. The flow of feedstock into the reactor is always accompanied with nitrogen flow unless stated otherwise. A condenser is used at the bottom of the reactor. Collected samples will consist of two phases because part of the products will be water which is insoluble in 1-decene and 1-decanol. Water in the products will have to be separated first before it can be analyzed using gas chromatography. The experimental setup system is illustrated in Fig 1.



No.	Unit
1	Gas regulator
2	Pump
3	Flow meter
4	Stainless Steel Reactor
5	Controller/Thermocouple
6	Split –Furnace
7	Catalyst Bed

Operating Conditions		
Temperature	300-350	°C
Pressure	1	atm
WHSV (feed)	0.5-6	h ⁻¹
Size of catalyst	1-1.8	mm

Figure 1 Experimental set up and operating conditions

The liquid effluent was analyzed using Agilent GC analyzer with a FID detector and a DB 1 column. In this report the calculated value of conversion (%) and selectivity (wt%) toward a particular substance will be used from time to time. Conversion is referred to as the percentage of the feedstock that is consumed or converted by the reaction. While, the value of selectivity is used to indicate how much of each product is formed based on the total amount of product and excluding the unreacted 1-decanol. Yield (wt%) is the composition of the product including the unreacted 1-decanol.

Results, Discussion and Conclusion

The major products formed during dehydration of 1-decanol were 1-decene and di-*n*-decyl ether. One side-reaction that occurs simultaneously is the double bond migration or also known as the internal isomerization, which produces internal olefins.

The effect of the flow of nitrogen gas was studied under the condition of feedstock flow in 0.08mL/min and temperature at 310°C. Fig. 2 demonstrated that the conversion of 1-decanol at different flow rate of 1-decanol was higher when nitrogen was used as a carrier gas (presence of inert gas). According to table 1, there was a reduction in the selectivity toward 1-decene when nitrogen gas was not flowing into the reactor (absence of inert gas). Moreover, as shown in Fig.3a, an increase in the selectivity of di-*n*-decyl ether was realized as the flow rate of 1-decanol is increased. However, according to Fig.3b when nitrogen gas is

flowing into the reactor only trace amount of di-*n*-decyl ether was detected. Therefore, it can be stated that a flow of nitrogen gas increases the formation of 1-decene, while minimizing the formation of di-*n*-decyl ether at higher flow rate of 1-decanol.

Table 1 Conversion of 1-decanol and product distribution in the dehydration of 1-decanol

	Feed (wt%)	Products Distribution (wt%)	
		Absence of inert gas	Presence of inert gas
Conversion	-	86.0	97.9
1-Decanol	100.0	14.0	1.7
1-Decene	-	25.6	55.3
Internal Olefins	-	59.8	42.9
Di- <i>n</i> -decyl ether	-	0.5	0.0

1-Decanol flow rate, 0.08 mL min⁻¹; Temperature, 310°C

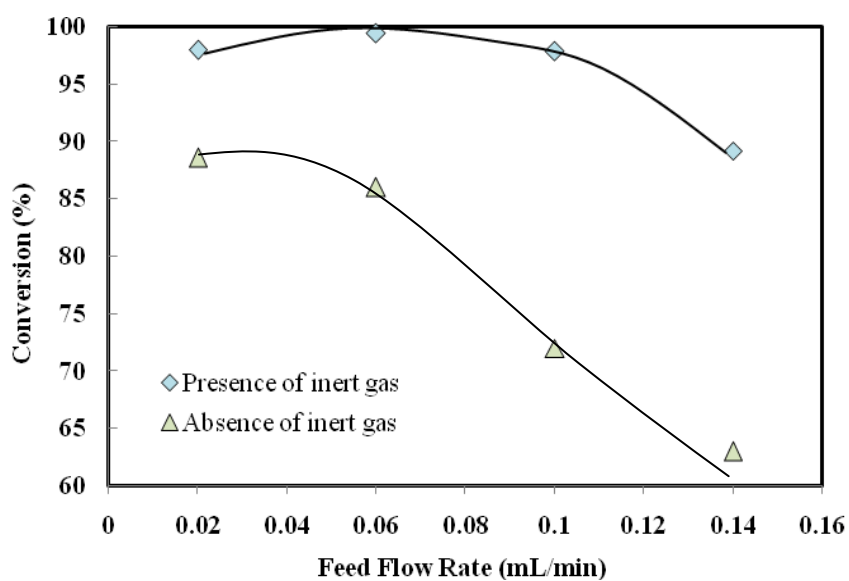


Figure 2 Effect of a flow of nitrogen as a carrier gas on the conversion of the dehydration reaction

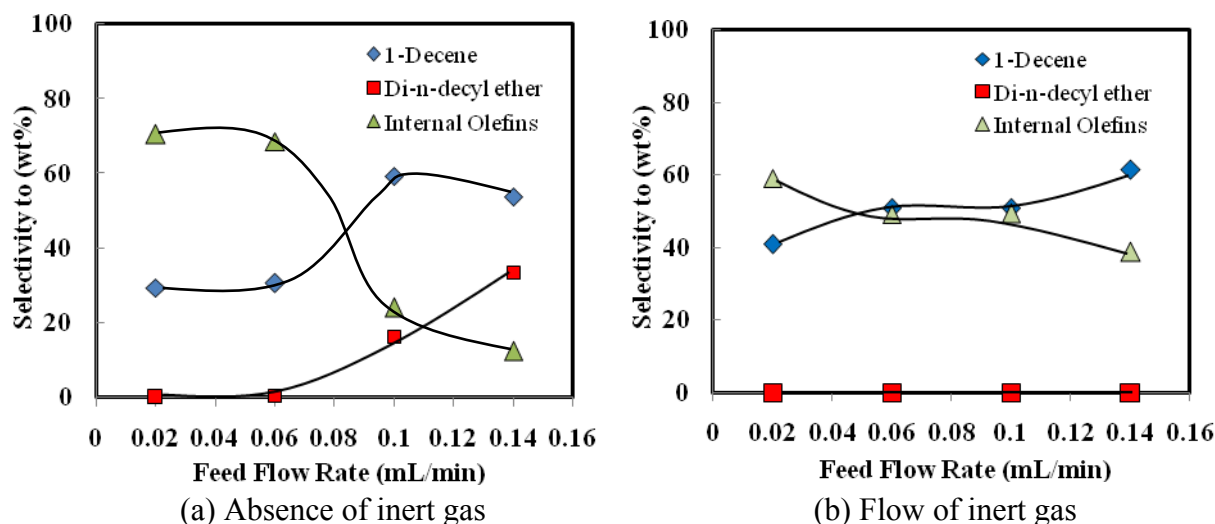
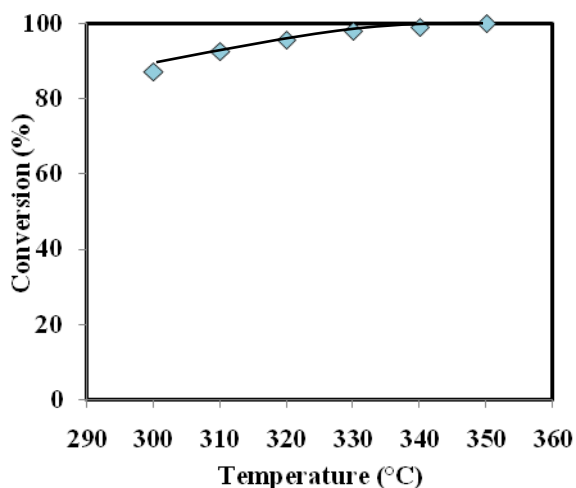


Figure 3 Effect of 1-Decanol flow rate on selectivity towards 1-decene, di-*n*-decyl ether, and internal olefins at 310°C. Absence of inert gas (a) and presence of inert gas (b)

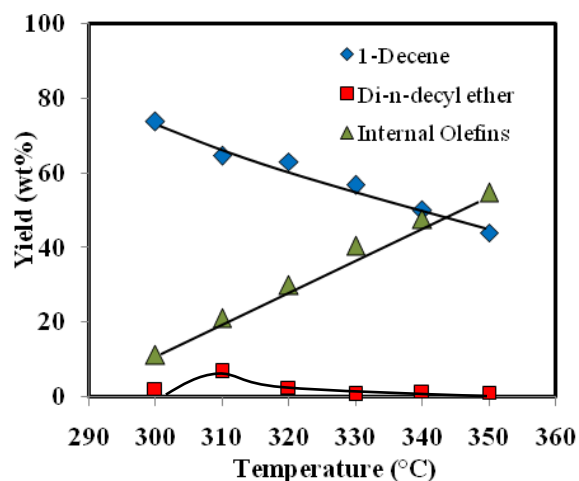
The effect of the temperature varying from 300 °C to 350 °C on the conversion of 1-decanol was studied under atmospheric pressure. As shown in Fig.4, conversion and the amount of internal olefin is increased with the temperature of the reaction. On the other hand, the composition of 1-decene in the product is gradually reduced with temperature. The formation of di-*n*-decyl ether reaches its peak at 310°C and then decreases toward zero at higher temperatures. Generally, the main products of dehydration of alcohols over γ -Al₂O₃ are olefins, but internal olefins as by-products are increased at higher conversion. Therefore, in order to avoid formation of internal olefins and optimize the production of 1-decene, the conversion will have to be lower than 100%. In the real production of 1-decene, unreacted 1-decanol can be separated from the product by means of distillation because the boiling point of 1-decanol is 230°C while the boiling point of 1-decene is only 175°C. However, it is quite difficult to separate 1-decene from its internal olefin because their boiling points are almost the same. Therefore, the operating condition used to optimize the generation of 1-decene is controlled by maintaining conversion at an appropriate level to avoid formation of internal olefin.

Table 2 Effect of temperature on selectivity towards 1-decene, di-*n*-decyl ether and internal olefins

Temperature (°C)	Selectivity to (%)		
	1-Decene	Di- <i>n</i> -decyl ether	Internal Olefins
300	84.56	2.61	12.83
310	69.74	7.38	22.88
320	65.98	2.79	31.23
330	58.01	0.76	41.23
340	50.41	1.54	48.05
350	43.97	1.28	54.74



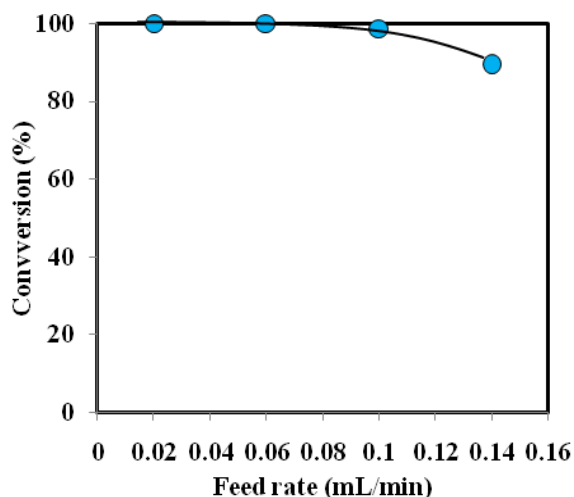
(c) Conversion of 1-decanol



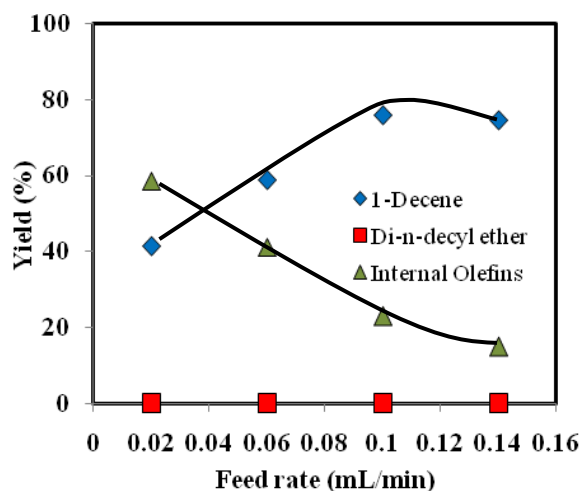
(a) Yield of products

Figure 4 Effect of temperature on conversion (a) and yield (b) at 1-decanol rate of 0.1 mL/min

The effect of feed rate of 1-decanol was studied under 310°C and nitrogen gas flow rate of 50mL/min. Although conversion decreases with increasing flow rate of 1-decanol, the amount of 1-decene increases. According to Fig.5, the optimum amount of 1-decene in the product is 70%. It is fascinating to witness the reduction of internal olefin as the feed rate increases. This is beneficial to the experiment because the objective is to maximize the formation of 1-decene.



(a) Conversion of 1-decanol



(b) Yield of products

Figure 5 Effect of feed rate of 1-decanol (mL/min) on conversion (a) and yield (b) at 310°C

In conclusion, the operating condition that is used to optimize the production of 1-decene was at 310°C, flow rate of 0.1 mL/min and under the presence of nitrogen as the carrier gas. The formation of di-*n*-decyl ether was minimized by flowing nitrogen into the system. It is worth pointing out that the conversion to internal olefin is also reduced when nitrogen gas is used.



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