Etherification of isoamyl alcohol using Amberlyst®15 as an acid catalyst

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ABSTRACT

The present work reports on the production of di-isoamyl ether from the etherification of isoamyl alcohol, using the sulphonic resin Amberlyst®-15 (A-15) as a catalyst. Parameters such as temperature, reaction time and amount of catalyst were studied. Although the etherification reaction shows low conversions (9-18%), when glycerol is added to the reaction medium and an external pressure to the reaction system (3.5 atm), the conversion increases up to 40% and a yield up to 100% can be obtained towards di-isoamyl ether.

Keywords: Etherification; isoamyl alcohol; di-isoamyl ether; Amberlyst®-15; acid catalyst.

Eterificación de alcohol isoamílico utilizando Amberlyst®15 como catalizador ácido

RESUMEN

El presente trabajo informa sobre la producción de éter diisoamílico a partir de la eterificación de alcohol isoamílico, utilizando la resina sulfónica Amberlyst®-15 (A-15) como catalizador. Se estudiaron parámetros como la temperatura, el tiempo de reacción y la cantidad de catalizador. Aunque la reacción de eterificación muestra conversiones bajas (9-18%), cuando se añade glicerol al medio de reacción y una presión externa al sistema de reacción (3,5 atm), la conversión aumenta hasta el 40% y puede obtenerse un rendimiento de hasta el 100% en di-isoamil éter.

Palabras clave: Esterificación; alcohol isoamílico; di-isoamilete; Amberlyst®-15; catálisis ácida.

1. Introduction

The growing demand for biofuels around the world has resulted in an increase in bioethanol production. Countries such as the United States and Brazil top the list of major producers [1]. Colombia is also among the ten countries with the highest production of bioethanol, concentrating mainly on sugarcane [2]. In the process of obtaining bioethanol, it is also possible to generate alcohols of greater weight than ethanol, called fusel oil. This mixture, which is a by-product obtained through the fermentation of agricultural products such as beet, cones (sweet molasses), grains, potatoes, sweet potatoes, barley, rice and wheat [3], it contains mainly isoamyl alcohol in addition to isobutyl alcohol, ethyl alcohol, methyl alcohol and *n*-propyl [4]. Recently, fusel oil has been used directly in mixtures with gasoline to minimize the negative impacts of the emission of CO_2 into the environment [5-7].

Cataluña *et al.* [8], proposed a new use of fusel oil through the use of an adiabatic reactor for the etherification of *iso*-amylenes present in the C_5, the five-carbon isomer cuts in petroleum distillates and the iso-amyl alcohol found in the fusel oil of the alcohol industry. The physicochemical characteristics of the di-isoamyl ethers obtained with commercial kerosene were compared.

The results showed significant changes in physicochemical properties, such as a decrease in the freezing point and an increase in the oxidation reaction rate. The authors suggest that changes in physicochemical properties indicate a high potential for the use of di-isoamyl ether as aviation fuel or in formulations with kerosene of fossil origin.

Considering that isoamyl alcohol is a by-product that can be valorized for use in aviation fuel formulations, this study reports on the etherification of *iso*amyl alcohol using Amberlyst®-15 as a catalyst to obtain di-isoamyl ether.

2. Experimental section

2.1. Chemicals and catalysts

Isoamyl alcohol (99%) and glycerol (99%) were obtained from Fisher. Amberlyst® 15 (dry) ion-exchange resin was purchased from Across Organic.

2.2. Characterization of Amberlyst® 15

The surface area was determined by applying the BET equation to -196 °C nitrogen fisisorption isotherms measured in TriStar II plus equipment. The Amberlyst® 15 sample was degassed at 3 mTorr and 423 K for 12 h before analysis. Infrared spectra (FTIR) of pyridine were recorded on a Nicolet Magna 550-FT-IR spectrometer with a 2 cm^{-1} optical resolution. Amberlyst®-15 was first pressed into self-supporting wafers (diameter: 1.6 cm, ≈20 mg) and pretreated from room temperature to 150 °C (heating rate of 2.5 °C /min for 1 h under a pressure of 1.33 10^{-4} Pa) in an IR cell connected to a vacuum line. Pyridine adsorption takes place at 150 °C. After establishing a pressure of 133 Pa at equilibrium, the cell is evacuated at 150 °C to remove all physisorbed species. The amount of pyridine adsorbed on the Brønsted and Lewis sites is determined by

integrating the band areas at respectively 1545 cm^{-1} and 1454 cm^{-1} and using the following extinction coefficients: ε_{1545} = 1.13 and ε_{1454} = 1.28 cm.mol^{-1} [9].

Thermogravimetric analysis (TGA) results were acquired on a SDT Q600 TA instruments. Samples were heated in a flow of Ar gas (80 mL min^{-1}) from room temperature to 900 °C with a ramp rate of 5 °C min^{-1}.

2.3. Etherification of *iso*amyl alcohol and analysis

The etherification reaction was carried out in a batch glass reactor (25 mL). Stirring was set at 1200 rpm and the amount of isoamyl alcohol used was 12.0 g. The reaction temperature was fixed at 115 °C (or 90 °C) and samples were taken at the beginning of the reaction (30 min) and at 6 h (or 12, 24 h). The reaction products were analyzed by gas chromatography using a chromatograph model Agilent 6890, DB-WAX column and a FID detector and butanol (Sigma Aldrich) as internal standard. Analyses were carried out with temperature program from 90 to 240 °C (with a slope of 30 °C min^{-1}). *Iso*amyl alcohol response factor was determined by calibration performed with standard. The reaction products were identified by gas chromatography with mass detector, QP2010 ULTRA SHIMADZU with a DB-5MS column.

Isoamyl alcohol conversion (%) was calculated using the following equation:

$$\text{Isoamyl alcohol conversion (\%)} = \frac{\text{moles of reacted isoamyl alcohol}}{\text{moles of initial isoamyl alcohol}} \quad (1)$$

3. Results and discussion

3.1. Acidic properties of A-15 and thermal resistance

Table 1 shows the surface area and acidity determined by adsorption of pyridine. The Amberlyst® 15 solid exhibits a BET area of 53 m^2 g^{-1}, which is characteristic of this resin with pores in the macroporous range between 40 and 80 nm [10]. Regarding acidity, the resin has a value of 2.3 mmol H$^+$, which corresponds to half the acid value reported by Rohm & Hass (4.7 mmol H$^+$). This result is consistent with that reported by Nguyen et al. where they also obtain this acid value [11].

Table 1. Textural and acidic properties of Amberlyst® 15

Sample	S$_{BET}$	Acidity mmol ([H$^+$] g^{-1})	
		Brønsted	Lewis
A-15	53	2.3	0

Thermal stability study was carried out. Figure 1 show the TGA curve of Amberlyst® 15. The degradation of this resin proceeds in three steps: i) dehydration at 130 °C, ii) desulfonation at 235-330 °C and iii) oxidation of polymer at 330-555 °C, representing a weight loss of 60.7 % at 600 °C. When the resin dehydration stage begins, the structure collapses and, therefore, the manufacturer recommends a maximum operation of 120 °C. This makes the application of this resin as a catalyst, in reactions with relatively low temperatures.
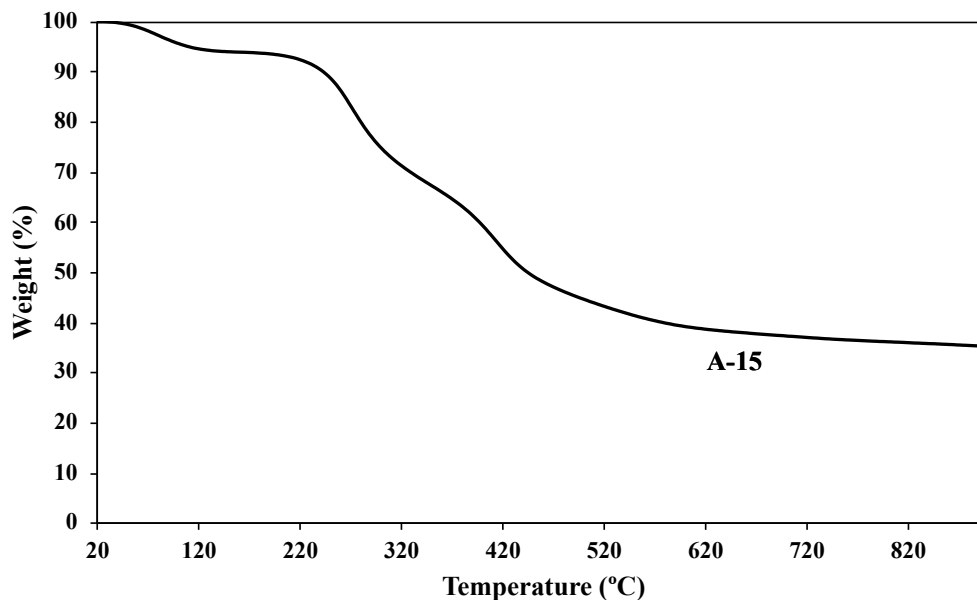
Figure 1. TGA pattern of A-15.

3.2. Etherification of *iso*amyl alcohol

To achieve the etherification of C5 alcohols, typically the reaction has been carried out by combining the isoamyl alcohol with C5 reactive olefins, reaching conversion values of up to 48% [8]. However, there are no reports of obtaining *iso*amyl ethers to date by direct etherification of *iso*amyl alcohol in the presence of acid catalysts. As this comprises the reaction of a "non-reactive" alcohol, it is expected that the presence of a Brønsted acid catalyst with the appropriate acid strength and concentration will be required in order to promote the reaction shown in Figure 2.
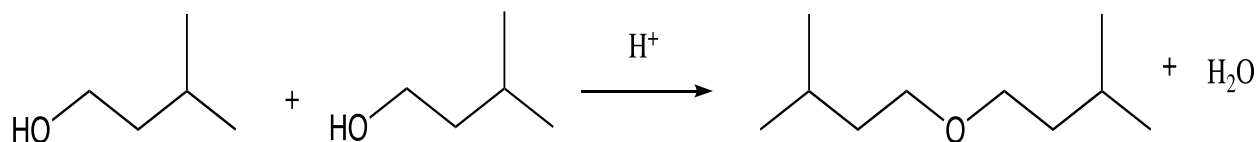

Figure 2. Etherification of isoamyl ether in presence of an acid catalyst

Initially, the etherification reaction of the isoamyl alcohol was carried out at 115 °C under magnetic stirring and without catalyst. The results after 24 hours showed no conversion. For this reason, Amberlyst® 15 was selected as a catalyst for this reaction. The results of the variation of the temperature, the amount of catalyst and the reaction time are presented below.

Effect of reaction temperature

To examine whether the increase in temperature affects the etherification reaction, two experiments were performed at 90 and 115 °C, where the latter is the maximum operating temperature that Amberlyst®15 resists without altering its structure (Figure 1). The results show that at 115 °C, it is possible to obtain a conversion greater than at 90 °C, for this reason the highest temperature was selected in this study, Figure 3.
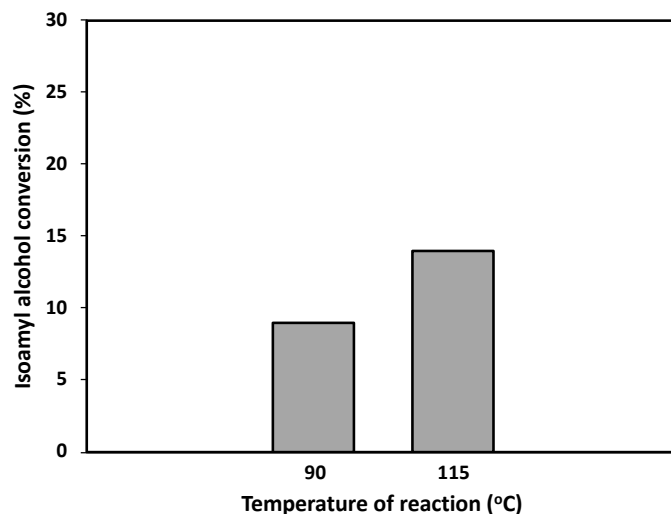
Figure 3. Effect of reaction temperature in the etherification of *iso*amyl alcohol.

Effect of the amount of catalyst

To examine the effect of the amount of catalyst on the etherification of *iso*amyl alcohol, the conversion obtained from alcohol was evaluated using 1 and 3 percent of Amberlyst®15 (with respect to the *iso*amyl alcohol). Figure 4 shows the results using the least amount of catalyst (1%), where an alcohol conversion of 13% was obtained. With a 3% catalyst, the conversion of *iso*amyl alcohol was 14%. Based on these results, 3% catalyst was initially selected as the most appropriate amount where it can be considered as a relatively low amount.
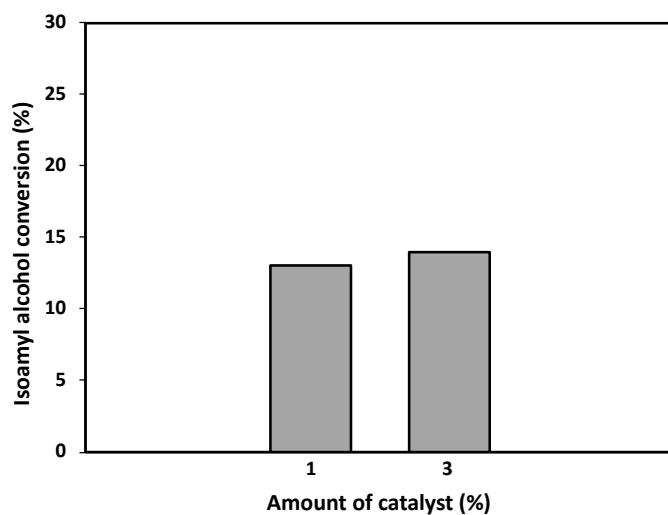

Figure 4. Effect of the amount of catalyst in the etherification of *iso*amyl alcohol.

Effect of reaction time

Once the most suitable percentage of catalyst was established, the reaction time was examined. In Figure 5, the results are shown with 6, 12 and 24 hours of reaction. According to the results, a reaction time greater

than 6 hours does not generate large amounts of conversion, which shows that the activity of this reaction is very low (TOF = 1.12 x10^{-1} h^{-1}).
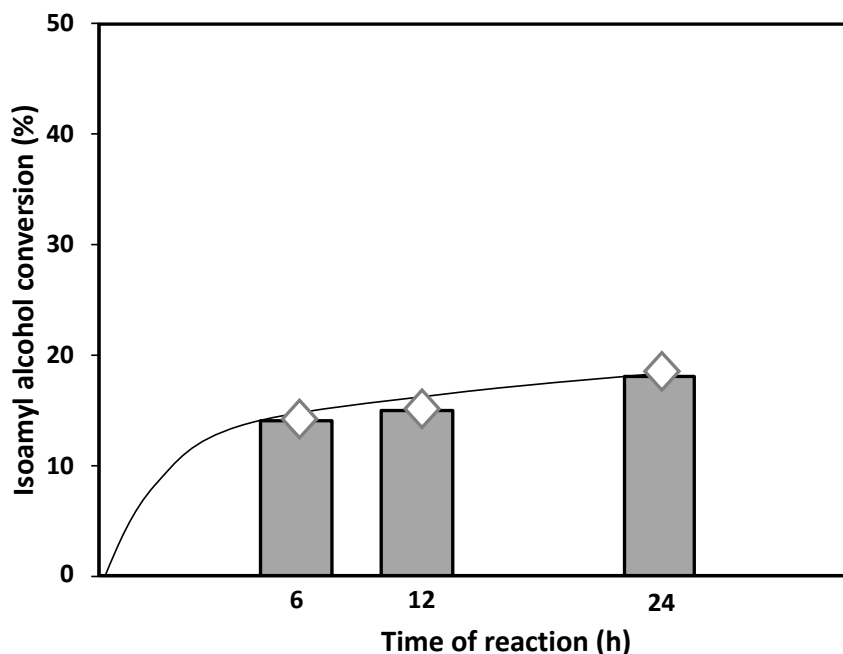

Figure 5. Effect of reaction time in the etherification of *iso*amyl alcohol.

According to Figure 5, a "semi-plateau" is observed after 6 hours of reaction, indicating a possible deactivation of the catalyst by the presence of water formed as a byproduct. For this reason, we decided to add glycerol, which is not miscible with isoamyl alcohol, and if it is capable of solubilizing water. Thus, in the reaction there were two different phases: i) glycerol + water and ii) isoamyl alcohol + isoamyl ether. In addition, the reaction system was brought to 3.5 atmospheres (by the addition of nitrogen). The conversion results and yield percentage are shown in Table 2.

Table 2. Etherification of isoamyl alcohol under different conditions

Reaction	Isoamyl alcohol Conversion (%)	Yield (%)
1[a]	18	>99
2[b]	22	>99
3[c]	40	100

[a] 12.0 g of isoamyl alcohol, atmospheric pressure (0.88 atm), 1200 rpm, 3% of catalyst, 115 ºC and 6 h of reaction. [b] 12.0 g of isoamyl alcohol, 3.1 g of glycerol, atmospheric pressure (0.88 atm), 1200 rpm, 3% of catalyst, 115 ºC and 6 h of reaction. [c] 12.0 g of isoamyl alcohol, 3.1 g of glycerol, 3.5 atm, 1200 rpm, 3% of catalyst, 115 ºC and 6 h of reaction.

The etherification reaction of isoamyl alcohol in the presence of Amberlyst®15 can be understood by the protonation of the hydroxy group of an alcohol molecule, followed by the removal of water and subsequent formation of a carbocation. A second molecule of alcohol, can produce a nucleophilic attack on that species generating the di-isoamyl ether. Figure 6 shows the possible reaction mechanism.
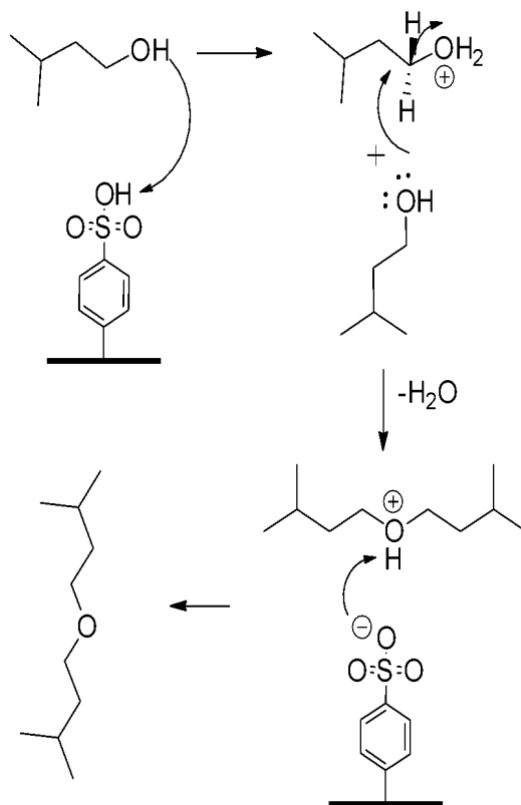
Figure 6. Proposed mechanism for the generation of isoamyl ether from isoamyl alcohol.

According to the results shown in Table 2, water extraction by adding glycerol improves the conversion by 4% compared to the initial reaction (without glycerol). When the system pressure increases 4 times, the conversion is double, achieving a conversion of 40%. These results suggest that it is possible to achieve a significantly better conversion in the etherification of isoamyl alcohol, removing water from the reaction medium and with the addition of pressure.

Stability of the catalyst

Due to the effects of pressure, the use and stirring temperature limit, the Amberlyst® 15 structure, which is initially in the form of small spheres, collapsed, making it impossible to reuse this reaction in the same initial conditions. However, when this collapsed solid is used in a second reaction cycle after washing with a mixture of methanol-acetone and drying at 70 ° C for 12 hours, a decrease in conversion (36%) was found. This proves that sulfonic groups can continue to promote the reaction despite the loss of the physical form that the acidic resin initially had.

4. Conclusion

The isoamyl ether was obtained from the etherification of the isoamyl alcohol by using Amberlyst® as a catalyst. The best results were presented using 3% of the solid, 115 ° C for 6 hours of reaction. Water extraction, which is a byproduct, improves conversion results. Also, the inclusion of pressure in the reaction system generates a positive effect since up to 40% conversion was obtained.

Contributions of the authors

Acknowledgments

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