Dehydrocondensation of 1-hexanol to di-n-hexyl ether (DNHE) on Amberlyst 70
Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

# Dehydrocondensation of 1-hexanol to di-n-hexyl ether (DNHE) on Amberlyst 70

E. Medina, R. Bringué, J. Tejero, M. Iborra, C. Fité, J.F. Izquierdo, F. Cunill

*Department of Chemical Engineering. University of Barcelona. Martí i Franquès, 1. E—08028-Barcelona. Spain.*

## Abstract

Conversion, selectivity, yield and kinetics of 1-hexanol liquid phase dehydrocondensation to di-n-hexyl ether (DNHE) were determined at 150-190 ºC on the thermally stable resin Amberlyst 70 in a batch reactor. At 190ºC, 1-hexanol conversion of about 71 %, with selectivity to ether of 87 % was obtained after 6-h reaction time. A kinetic model stemming from an Eley-Rideal mechanism in which 1-hexanol from the liquid phase reacts with 1-hexanol adsorbed on a single centre to give water adsorbed on a single site represents data suitably. Activation energy was computed to be 130 kJ/mol

Keywords: di-n-hexyl ether, 1-hexanol, Amberlyst 70, dehydrocondensation reaction.

## 1. Introduction

After sweeting diesel streams decreasing its sulfur content, formulation of future diesel fuels will be characterized by higher cetane number; decreasing at the same time its density and aromatics content [Douad, 1995] Unfortunately due to huge oil demand, heavy crudes amounts processed in refineries are increasing and total quantity of such compounds increases. Refineries has made an effort introducing hydrocracking units in order to decrease sulphur content and obtain high added value products from heavy streams. In addition, legislation is in continuous evolution, and a hypothetical change in cetane number specifications would help to decrease particle matter emissions as well as CO, $NO_x$, unburned hydrocarbons and smoke. [Giavazzi et al., 1991; Van Heerden et al., 1998]

A possible option of reformulating diesel blends is the introduction of oxygenates in commercial blends. Previous studies concluded that linear ethers with at least 10 carbon atoms showed high cetane numbers and desirable cold flow properties [Pecci et al., 1991].

Di-n-hexyl ether (DNHE) has been selected to carry out the present study since it itself behaves as a light diesel fuel. Boiling point of DNHE is about 220ºC, closer to light end of commercial boiling point of diesel fuels (200ºC - 380ºC). Density and viscosity of DNHE are actually lower than that of standard diesel fuels. However, since cetane number of DNHE is as high as 118, its introduction in commercial blends contributes to upgrade diesel properties particularly in the light end of the boiling point curve [Olah, 1996].

Oil industry is interested in increasing the cetane number of low quality diesel streams, i.e. linear $C_5$ olefins. The production of high cetane ethers from linear olefins could be a promising way. To do this, 1-hexanol may be synthesized by hydro-formylation of 1-pentene, a feedstock of $C_5$ olefin streams. The industrial synthesis consists of selective hydroformylation and hydrogenation of 1-pentene in the presence of rhodium and cobalt phosphines [Hagen, 1999]. After, the molecular dehydration reaction of the alcohol gives DNHE. The alcohol dehydration reaction needs an acid catalyst to proceed. Ion exchange resins are today the best option (in terms of selectivity and activity) to achieve good yields in ether [Patrini and Marchionna, 1998; Karpov et al., 1967; Swistak and Mastagli, 1954].

In previous works, acidic ion exchange resins have shown to be highly selective to the ether formation, avoiding secondary reactions, i.e. dehydration to olefin. Recently, thermally stable ion exchange resins based on styrene-divinylbenzene copolymers have been commercialized, i.e. Amberlyst 70. Amberlyst 70 has shown to be an effective catalyst in 1-pentanol dehydration to di-n-pentyl ether (DNPE) [Tejero et al., 2002; Bringué et al., 2006]. In fact, compared to Nafion NR50, Amberlyst-70 was much more active than Nafion catalyst, but only a bit less selective.

In the liquid phase, DNHE synthesis on thermally stable ion exchange resins is only reported in the presence of NR50 [Olah et al., 1997]. So, present work is devoted to the study of the reaction of dehydration of 1-hexanol to DNHE on Amberlyst 70. Synthesis of DNHE and DNPE on this resin will be compared. Finally, a preliminary kinetic study was performed.

## 2. Experimental

*Materials.* 1-hexanol (99.5% pure, < 0.3% 2-methyl-1-pentanol, 0.1% water) was used after purification in a distillation column of the alcohol supplied by Fluka ($\geq$ 98%). Di-*n*-hexyl ether was obtained in our lab and purified to $\geq$ 98%. 1-hexene ($\geq$ 99%) from Aldrich, *trans*-2-hexene ($\geq$ 98%), *cis*-2-hexene ($\geq$ 95%), *trans*-3-hexene ($\geq$ 97%), *cis*-3-hexene ($\geq$ 95%), and 2-methyl-1-pentanol ($\geq$ 99%) were supplied by Fluka and used for analysis purposes.

The catalyst was the thermally stable acidic resin Amberlyst 70, a chlorinated low crosslinked polystyrene-divinylbenzene (PS-DVB) copolymer from Rohm and Haas France. Amberlyst 70 (A-70) has an acidic capacity of 3.01 meq $H^+$/g, an skeletal density of 1.52 g/cm$^3$, mean bead diameter of 570 nm, and its maximum operating

temperature is 200ºC [Collin and Ramprasad, 2004]. Its structural properties are given in table 1.

Table 1. Structural properties of Amberlyst 70 (A70).

| Dry state [a] | | | | |
|---|---|---|---|---|
| $S_g^b$ (m$^2$/g) | $V_g^c$ (cm$^3$/g) | $d_{pore}^d$ (nm) | $\theta^e$ (%) | |
| 30 | 0.153 | 19,3 | 18.8 | |
| Swollen in water (ISEC method) | | | | |
| $S_g$ (m$^2$/g) | $V_g$ (cm$^3$/g) | $V_{sp}$ (cm$^3$/g) | $d_{pore}^d$ (nm) | $\theta^e$ (%) |
| 176 | 0.355 | 8.1 | 1.19 | 57.4 |

a) Dried by successive percolation with methanol, toluene and isooctane.
b) BET method.
c) Determined by adsorption-desorption of $N_2$ at 77 K.
d) Assuming pore cylindrical model.
e) In dry state $\theta = 100 \, V_g/(V_g+(1/\rho_s))$. Swollen in water, $\theta = 100(V_g+V_{sp}-(1/\rho_s))/ (V_g+V_{sp})$.

Amberlyst 70 is a macroporous resin flexible enough to accommodate to aqueous media because of its low crosslinking degree. This fact is stated by the determination of bead size made in water, DNHE, 1-hexanol and air by a laser technique with a Microtrack SRA analyser. Figure 1 show that beads swell clearly in water, but hardly swells in alcohol and ether. The same fact is observed in Inverse Steric Exclusion Chromatography (ISEC) structural measurements in water (Table 1) [Jerabek, 1996]
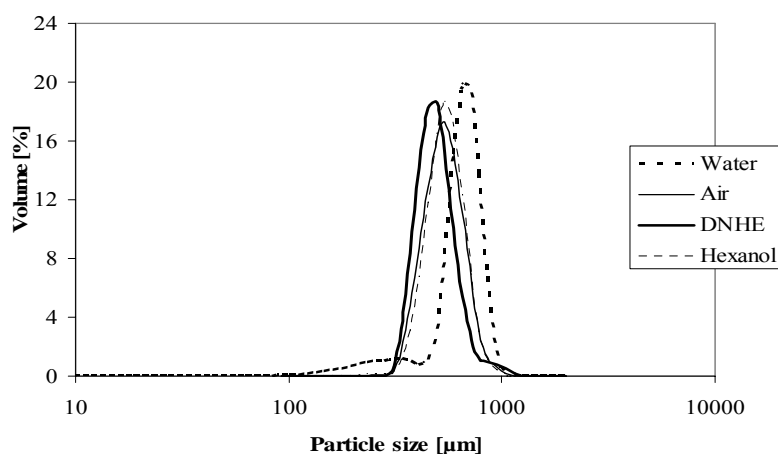


Fig. 1. Distribution of bead size in different liquid media.

***Experimental set-up***. Experiments were carried out in a 100-mL stainless steal autoclave which operates in batch mode. A magnetic drive turbine was the mixing system. Temperature was controlled to within ±1 K by an electric furnace. To carry out the reaction in the liquid phase pressure was set at 2.1 MPa using $N_2$ as inert gas. One of the outlets of the reactor was connected directly to the liquid sampling valve, which injected 0.2 µl of pressurized liquid into a GLC apparatus.

***Analysis.*** The composition of liquid mixtures was analyzed by using a split-mode operation in a HP6890A GLC apparatus equipped with TCD, because of the presence of water as a reaction product. A 50 m x 0.2 mm x 0.5 μm methyl silicone capillary column was used to determine 1-hexanol, DNHE and by-products: $C_6$ olefins (1-hexene, 2-hexene and 3-hexene) and branched ethers (2,2-oxibis hexane and 1,2-oxibis hexane). The column was temperature programmed with a 6 min initial hold at 45ºC, followed by a 30 ºC/min ramp up to 180ºC and holding for 5 min. Helium was used as a carrier gas at a total flow rate of 30 ml/min.

***Methodology.*** Amberlyst 70 was dried at 110ºC in an oven. Firstly at atmospheric pressure 15 h, and then 2 h in vacuum. Dried catalyst and 70 ml of 1-hexanol were charged into the reactor and when pressure achieved 2.1 MPa leaking problems were checked, and the reactor heated until reaction temperature was reached. This time was taken as the zero time of experiment. For 6 h, liquid samples were analyzed hourly to obtain the variation in concentration over time of all compounds. The temperature was selected in the range 150 – 190ºC. The effect of stirring speed was studied among 50 and 800 rpm for two different stirrers: a six blade dispersimax and a four blades axial up disperser. Catalyst mass used was between 1 and 3.5 g.

In each experiment, 1-hexanol conversion ($X_h$), selectivity to DNHE ($S_{DNHE}$), to alkenes ($S_{alkenes}$) and to branched ethers ($S_{ethers}$), and yield of DNHE with respect 1-hexanol ($Y_{DNHE}$) were computed by the expressions.

$$X_{HeOH} = \frac{mole\ of\ 1-hexanol\ reacted}{initial\ mole\ of\ 1-hexanol} \tag{1}$$

$$S_{DNHE} = \frac{mole\ of\ 1-hexanol\ reacted\ to\ form\ DNHE}{mole\ of\ 1-hexanol\ reacted} \tag{2}$$

$$Y_{DNHE} = \frac{mole\ of\ 1-hexanol\ reacted\ to\ form\ DNHE}{initial\ mole\ of\ 1-hexanol} = X_{HeOH} S_{DNPE} \tag{3}$$

Finally, from the function of variation of $n_{DNHE}$ (number of DNHE moles produced) versus time, reaction rates of DNHE formation were calculated as:

$$r_{DNHE} = \frac{1}{W} \left( \frac{dn_{DNHE}}{dt} \right)_t \quad \left[ \frac{mol\ DNHE}{kg \cdot h} \right] \tag{4}$$

## 3. Results and discussion

### 3.1) Description of an experiment

First of all, it was checked if drying method changes the catalytic behaviour of A-70. To do this, catalyst was dried for 5, 15, 45 and 120 h in atmospheric oven at 110ºC followed by 2 h at vacuum oven. It was found that when catalyst was dried in atmospheric oven for more that 15 h, alcohol conversion and selectivity hardly changed. As a consequence this drying method was selected.

Figure 2 shows typical plots of DNHE and by products mole evolution on A-70 throughout an experiment conducted at 190ºC. Heating period when that temperature is reached was about 20 min. and alcohol conversion about 3.5%. From this time, the reaction proceeds smoothly. It is to be noted that, the amount of water in the liquid phase is lower than that DNHE, probably because preferential adsorption on the resin. On the other hand, by-products appear when the reaction begins, and their amount rises continuously through the experiment.
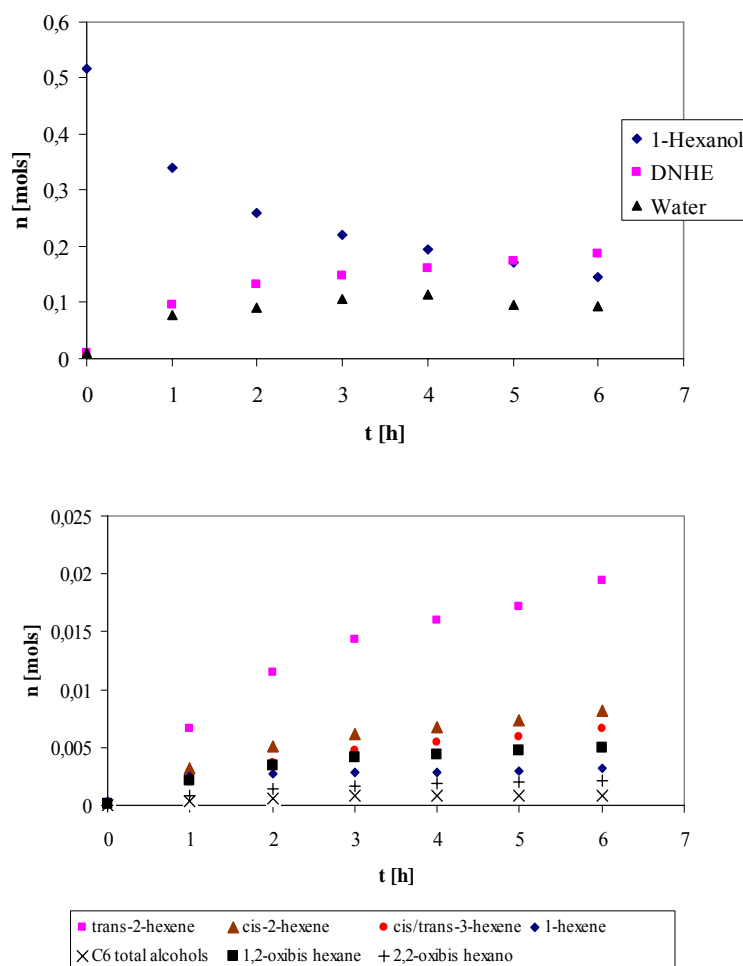


Fig.2. Variation of composition of the reaction medium with time at 170ºC on 1g of catalyst and 500 rpm (Up: 1-pentanol, DNHE, and water; down: by-products).

Detected by-products are $C_6$ olefins (1-hexene, *trans-* and *cis-*2-hexene, *cis/trans-*3-hexene), $C_6$ alcohols (2-hexanol and 3-hexanol) and $C_{12}$ branched ethers (1,2-oxibis hexane and 2,2-oxibis hexane). They were identified by means of GLC apparatus equipped with an MS detector. In the case of branched ethers, they were synthesized in our lab from the appropriate $C_6$ alcohols.
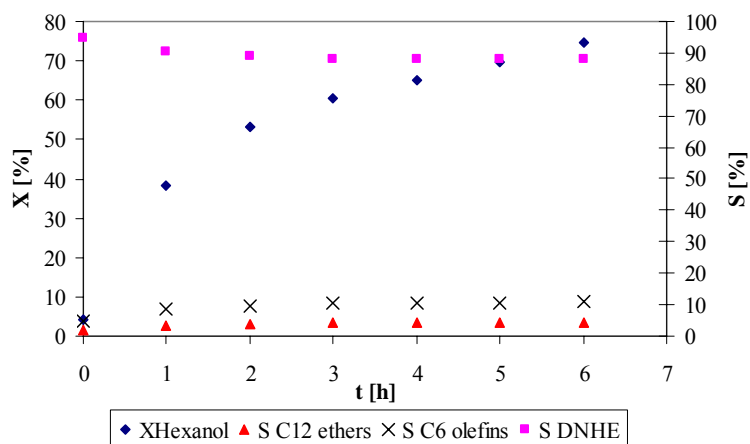


Fig. 3. Hexanol conversion and selectivity to DNHE, branched ethers and $C_6$ olefins (190ºC; 500 rpm; 1 g of Amberlyst 70)

Figure 3 shows the evolution of 1-hexanol conversion and selectivity through an experiment. As can be seen, selectivity to DNHE decreases with time as the reaction is approaching chemical equilibrium, whereas selectivity to olefins and branched ethers increases but very slowly. Selectivity to alcohols other than 1-hexanol is very low, and it is not shown in Figure 3.

Based on the evolution of the composition in the liquid phase, the following reaction scheme could be proposed:
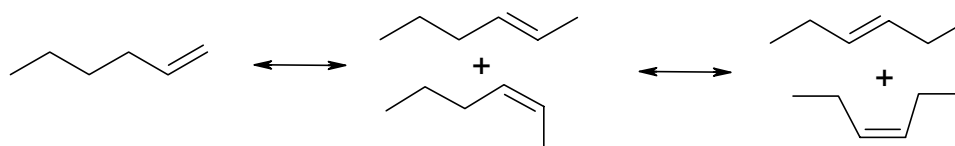
1) Dehydration of 1-hexanol to DNHE is the main reaction.
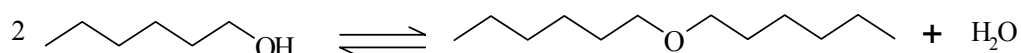


2) Dehydration to 1-hexene is the main side reaction,
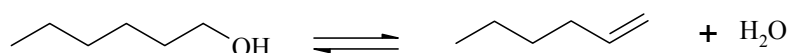


3) 1-hexene isomerizes to 2-hexene (*cis* and *trans*), and 3-hexene (*cis* and *trans*).



6

4)  Alkenes may react with water giving place to $C_6$ alcohols (2 and 3-hexanol). Finally, the reaction between the appropriate pair of alcohols give branched ethers: 2-hexanol gives place to 2,2-oxibis hexane; 2-hexanol and 1-hexanol react to give 1,2-oxibis hexane. Notwithstanding that, the reaction between the appropriate couple of olefin and $C_6$ alcohol could also give branched ethers, i.e. 1-hexene reacting with 1-hexanol to give 1,2-oxibis hexane.
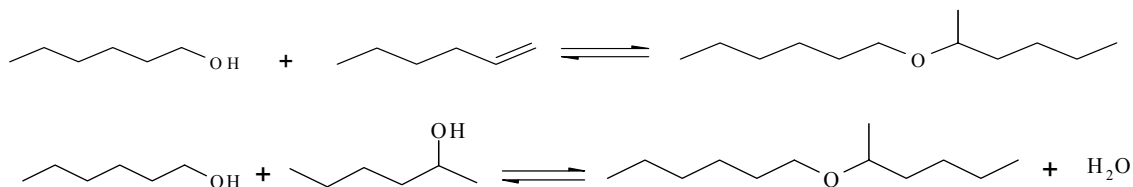
## 3.2) Preliminary experiments

Preliminary experiments were performed at 190ºC by studying the effect of catalyst mass, stirring speed and particle size on initial reaction rate. The effect of the catalyst mass was checked in a series of experiments carried out with catalyst amounts between 0.5 to 5 g. Figure 4 shows the influence of mass of A-70 on the measured initial reaction rate. As it is observed there is not catalyst mass influence of catalyst for amounts lesser than 3.5 g, within the limits of the experimental error. For higher catalyst mass initial reaction rate drops significantly, probably because with such amount of catalyst some external mass transfer limitations appear.
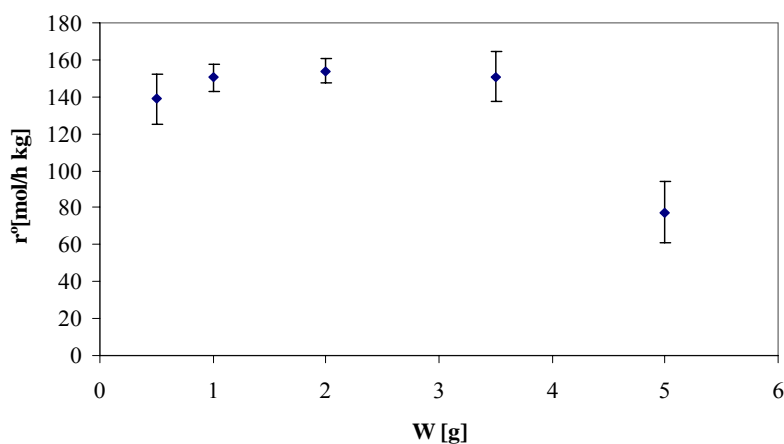
Figure 4. Effect of mass catalyst on the reaction rate at 190ºC and 500 rpm (commercial distribution of bead size).

The influence of external transfer mass was checked by using two different mixers. Firstly, a six blade Dispersimax impeller was used in the stirring speed range of 50 - 800 rpm. As Figure 5 shows, measured initial reaction rates were the same, within the limits of the experimental error, in the 100 - 600 rpm range. The same conclusion can be drawn when 1-hexanol conversions are compared. When a four blade axial up was used, it was seen that initial reaction rates hardly change between 100 and 800 rpm.

Also, alcohol conversions are the same, within the limits of the experimental error, between 200 and 800 rpm. As a result, stirring speed was set at 500 rpm in subsequent experiments using the 4-blade axial up mixer.
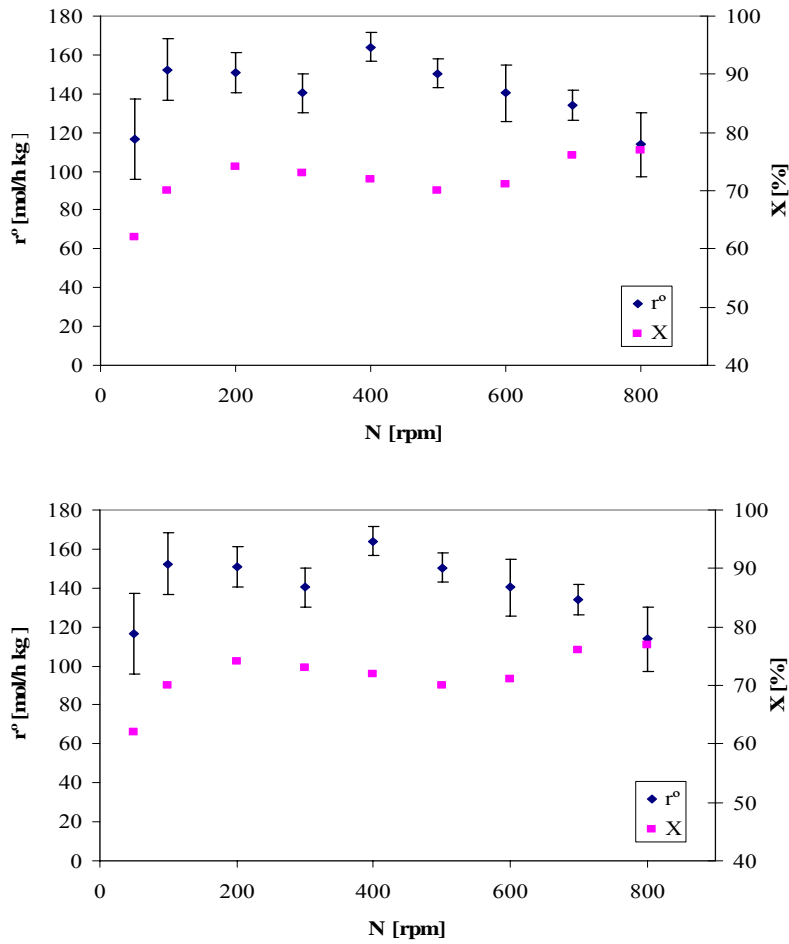




Fig. 5. Effect of stirring speed on hexanol conversion and initial reaction rate (commercial distribution of bead size; 1 g A-70). 6-blades dispersimax (up). 4-blade axial up mixer (down)
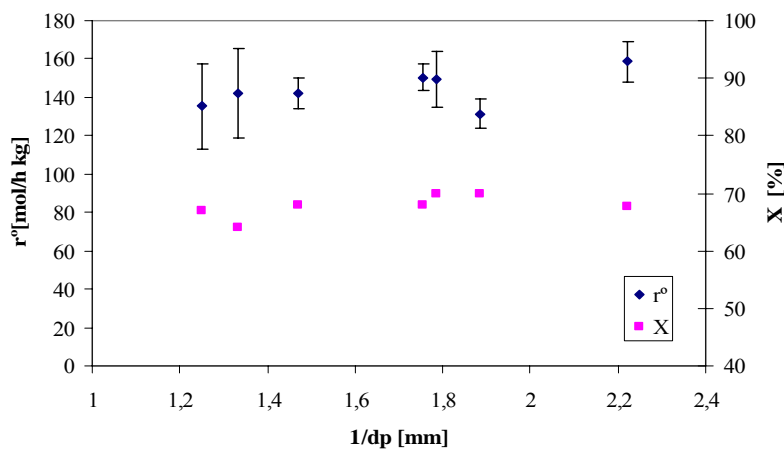


Fig. 6. Influence of particle size on initial reaction rate (T = 190ºC; 500 rpm; W = 1 g)

Finally, to assess the influence of catalyst size on the reaction rate, an experimental series was carried out at 190ºC and 500 rpm using beads of different particle size in the range 0.45 - 0.8 mm. As shown in Figure 6, initial reaction rate is not influenced by the resin particle size within the limits of the experimental error. Probably, this effect is due to resin swelling by the water produced in the reaction, favouring diffusion to the active sites. Mean value of particle size distribution of commercial beads is close to 0.57 mm, so henceforth samples with commercial particle distribution size was used.

## 3.3) Synthesis of DNHE: effect of temperature

To test the effect of temperature, a series of experiments was performed on A-70 at 150 – 190ºC and 500 rpm using 1 g of resin commercial beads. Table 2 shows 1-hexanol conversion and selectivity to DNHE and by-products after 6 h of reaction time. As can be seen, conversion increases with temperature and $S_{DNHE}$ decreases, as was expected, on the basis of our previous work on the synthesis of di-n-pentyl ether on Amberlyst 70 [Bringué et al., 2006]. $S_{DNHE}$ decreased with temperature due to the formation of $C_6$ alkenes. It is likely that branched ethers are formed by reaction between olefins and alcohols, since detected amounts of $C_6$ secondary and tertiary alcohols were extremely low. DNHE yields increase with temperature, as expected, despite $S_{DNHE}$ decreases with temperature, and a maximum DNHE yield of 71% is achieved at 190ºC with 1 g of catalyst, as can be seen in table 2.

Table 2. Conversion, selectivity, ether yield and initial reaction rate of dehydration of 1-hexanol to DNHE, and dehydration of 1-pentanol to DNPE on A-70.

| T(ºC) | $X_{HeOH}$ (%) | $S_{DNHE}$ (%) | $Y_{DNHE}$ (%) | $S_{alkenes}$ (%) | $S_{ethers}$ (%) | $r^0$ (mol/h.kg) |
|---|---|---|---|---|---|---|
| 150 | 16.5 | 97.7 | 16.1 | 1.5 | 0.8 | 10.7 |
| 160 | 29.7 | 96.2 | 28.6 | 2.4 | 1.4 | 18.7 |
| 170 | 47.6 | 94.3 | 44.9 | 3.5 | 2.1 | 32.3 |
| 180 | 63.7 | 91.1 | 58.0 | 5.9 | 3.0 | 73.3 |
| 190 | 70.9 | 86.9 | 61.7 | 9.4 | 3.6 | 151 |
| T(ºC) | $X_{PeOH}$ (%) | $S_{DNPE}$ (%) | $Y_{DNPE}$ (%) | $S_{alkenes}$ (%) | $S_{ethers}$ (%) | $r^0$ (mol/h.kg) |
| 150 | 13.7 | 97.8 | 13.4 | 0.9 | 1.3 | 8.1 |
| 160 | 25.1 | 96.8 | 24.3 | 1.6 | 1.6 | 15.6 |
| 170 | 41.8 | 95.5 | 39.9 | 2.4 | 2.1 | 33.6 |
| 180 | 54.1 | 93.0 | 50.3 | 4.1 | 2.9 | 48.7 |
| 190 | 67.7 | 90.8 | 61.4 | 5.8 | 3.4 | 112 |

It is interesting to compare the behaviour of Amberlyst 70 in the related synthesis of DNPE and DNHE since both ethers have been proposed as options to reformulate diesel fuels. Compared to the dehydration of 1-pentanol performed in the same set-up [Bringué et al., 2006], DNHE synthesis on this resin is a bit faster but less selective to ether. However, yields in ether are of the same order (Table 2). These facts suggest that both reactions could be suitable means to upgrade $C_4$ and $C_5$ olefins by synthesizing valuable linear ethers

## 3.4) Kinetic study of the reaction.

As table 2 shows the reaction of synthesis of DNHE is quite sensitive to temperature, since in the temperature range studied initial reaction rate becomes twice when reaction temperature increases 10ºC. To do a kinetic study of the reaction, since measured reaction rates are confident if catalyst mass lower than 3.5 g is used, the experimental design described in the previous point was completed with additional experiments done at the same temperatures but using a catalyst mass of 2 and 3.5 g.

In order to show that experiments performed with different catalyst weight are consistent, at each temperature conversion data were plotted against the parameter $W \cdot t/n_{H,0}$. According to the performance equation of a batch stirrer reactor in the absence of artefacts all data have to be distributed along a unique curve. As it is seen in Figures 7 to 11, all the experiments are consistent.
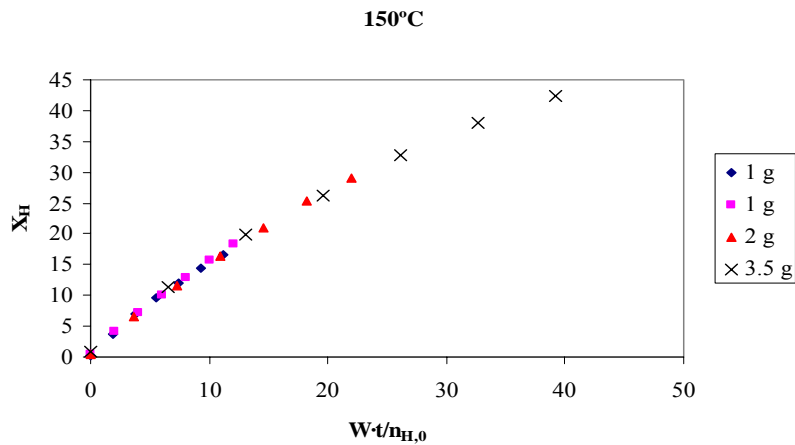
**150ºC**



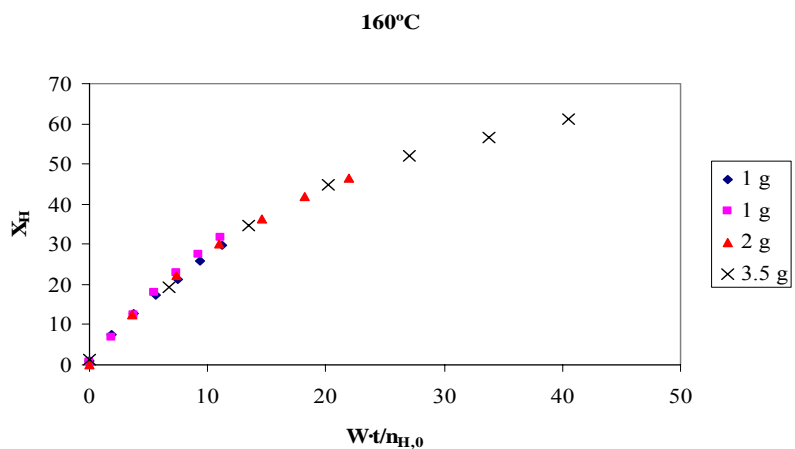Fig. 7. Plot of 1-hexanol conversion against $W \cdot t/n_{H,0}$ at 150 ºC

**160ºC**



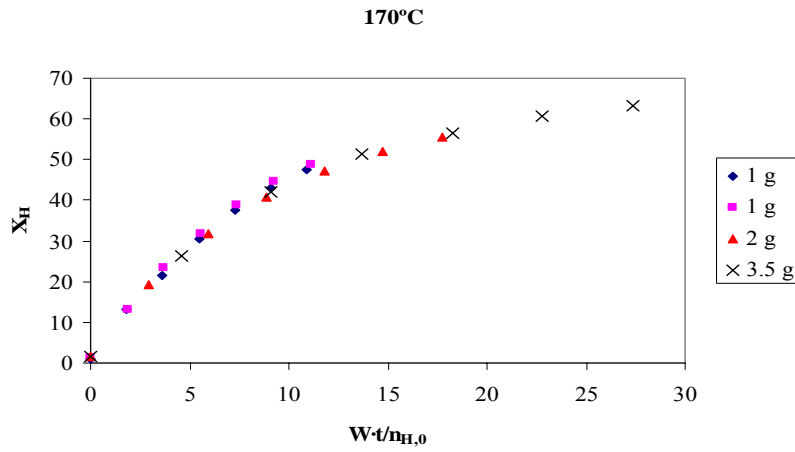Fig. 8. Plot of 1-hexanol conversion against $W \cdot t/n_{H,0}$ at 160ºC

**170ºC**



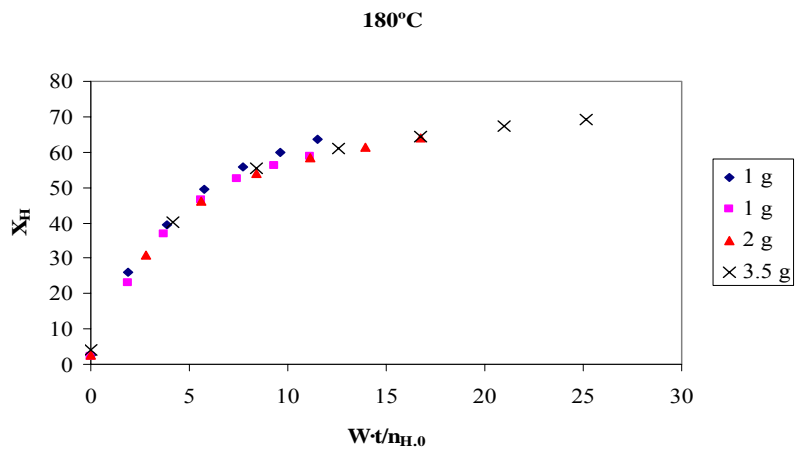Fig. 9. Plot of 1-hexanol conversio against W.t/n$_{H,0}$ at 170ºC

**180ºC**



Fig. 10. Plot of 1-hexanol conversio against W.t/n$_{H,0}$ at 180ºC
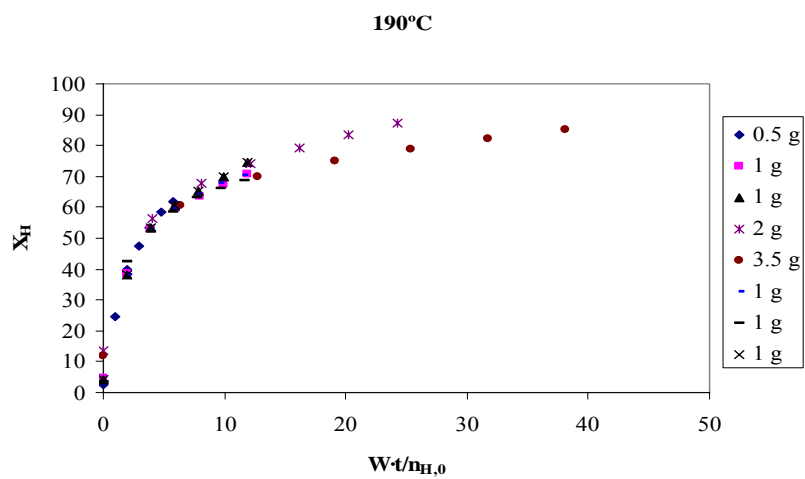
**190ºC**



Fig. 11. Plot of 1-hexanol conversion against W.t/n$_{H,0}$ at 190ºC

From a molecular point of view two possible mechanisms for the reaction of DNHE synthesis can be looked up [Bringué et al., 2006]. The first one involves the in situ formation of an oxonium ion, which is a good leaving group, by protonation (specific acid catalysis). The ether would be formed by the nucleophilic attack of alcohol on the oxonium ion in a S$_N$2 bimolecular reaction. Dehydration to 1-hexene follows a monomolecular dehydration (E1) and due to its reactivity, isomerization to 2 and 3 hexene takes place when the olefin appears. However, when there is little water in the system or the alcohol is in a great excess, the reaction could take place by the initial reaction of 1-hexanol at sulfonic groups to form 1-hexylsulfate (general acid catalysis). Then, the ether would be formed by the attack of a second molecule of alcohol on the sulphate in a S$_N$2 reaction as well.

The first mechanism is in agreement with a Langmuir-Hinshelwood-Hougen-Watson kinetic one, in which two adsorbed molecules of alcohol take part. Assuming that surface reaction is the rate controlling step, the following kinetic model is obtained:

$$r = \frac{\hat{k} \cdot K_{a,H}^2 \cdot \left( a_H^2 - \dfrac{a_D \cdot a_W}{K_{eq}} \right)}{\left( 1 + K_{a,H} \cdot a_H + K_{a,D} \cdot a_D + K_{a,W} \cdot a_W \right)^2} \tag{5}$$

On the contrary, the second mechanism is in agreement with an Eley-Rideal kinetic one, in which a molecule of alcohol from the liquid phase reacts with an adsorbed alcohol molecule. By assuming that surface reaction is the rate controlling step, and DNHE is released directly to the liquid, the following kinetic model is obtained

$$r = \frac{\hat{k} \cdot K_{a,H} \cdot \left( a_H^2 - \dfrac{a_D \cdot a_W}{K_{eq}} \right)}{\left( 1 + K_{a,H} \cdot a_H + K_{a,W} \cdot a_W \right)} \tag{6}$$

Since the system behaves no ideally, concentrations of reactant and products have been expressed in terms of activities. Activity coefficients were estimated by using the UNIFAC-DORTMUND method [Wittig and Lohmann, 2003].

Equations 5 and 6 were fitted to data, as well as simplified models obtained by assuming that adsorption of alcohol, ether or water was negligible. Since the variation of equilibrium constant with temperature was unknown, equilibrium constant was obtained by fitting of data to kinetic equations.

The best model from a statistical standpoint (minimum sum of squares, random residuals and low parameter correlation) with physicochemical meaning (positive activation energy and negative adsorption enthalpies and entropies) is the following:

$$r = \frac{\hat{k} \cdot K_{a,H} \cdot \left( a_H^2 - \dfrac{a_D \cdot a_W}{K_{eq}} \right)}{\left( 1 + K_{a,H} \cdot a_H + K_{a,W} \cdot a_W \right)} = \frac{\hat{k} \cdot \left( a_H^2 - \dfrac{a_D \cdot a_W}{K_{eq}} \right)}{a_H + \left( K_{a,W} / K_{a,H} \right) \cdot a_W} \tag{7}$$

where $\hat{k} = \exp\left[ k_1 - k_2 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right] = \exp\left[ 3.61 - 1.57 \cdot 10^4 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right]$ (8)

$$K_{eq} = \exp\left[ k_3 - k_4 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right] = \exp\left[ 0.275 - 8.59 \cdot 10^3 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right] \tag{9}$$

and $\quad \dfrac{K_{a,W}}{K_{a,H}} = \exp\left[ k_5 - k_6 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right] = \exp\left[ 0.062 - 8.94 \cdot 10^3 \left( \dfrac{1}{T(K)} - \dfrac{1}{443.15} \right) \right]$ (10)

As Figure 12 shows, equation 7 fits rate data fairly well in the whole temperature range explored, despite that a very slight trend appear at low temperatures (150-170 ºC). By comparing equation 8 with the Arrhenius one it can be deduced that parameter $k_2 = E_a/R$. So from the value of $k_2$ an activation energy of 130 KJ/mol was estimated. There is not activation energies reported in literature for DNHE on ion-exchange resins yet, however this value is a bit higher that the value of $119 \pm 4$ reported for the reaction of dehydration of 1-pentanol to di-n-pentyl ether (DNPE) on A-70 [Bringué et al. 2006].

Parameters $k_5$ and $k_6$ of equation 10 supply information on the difference between adsorption enthalpies and entropies of ether and alcohol respectively. So, $\Delta H_W - \Delta H_H$ and $\Delta S_W - \Delta S_H$ were computed to be respectively, 74.3 kJ/mol and 168 e.u..

Finally, from parameter $k_4$, the reaction enthalpy was estimated to be about 71.4 kJ/mol (endothermic). This in an unreliable value since reactions of dehydration of alcohol to ether are slightly exothermic. This artifact could be explained because the range of 1-hexanol conversions is very short at the low temperatures of the range explored (see Figures 7 to 9). As a result, in the process of data fit, dependence on temperature of $K_{eq}$ appears to be abnormally high.

Equation 7 fits data reasonably well. However, as a consequence of the inconsistency of fitted $K_{eq}$ upgrading of the kinetic model is necessary. To do that, further work will be addressed to obtain the temperature dependence of $K_{eq}$ from direct measurements of chemical equilibrium composition at different temperatures. Also, the effect of water on the kinetics would be ascertained. Water swells the resin as it is formed (see Figure 1) and favours that reaction takes place in the entire resin bead. Also, it adsorbs on the resin lessening reaction rate. However, by comparing with the 1-pentanol-DNPE-water system, some important differences are seen. In the synthesis of DNPE, water adsorbed prevented the alcohol to adsorb on the sulfonic groups, and as a consequence reaction took place only in the fraction of acid centers free of water,

but water adsorption was not significant in the denominator of kinetic equation. These differences may be explained by the different ether and alcohol concentrations range studied. However, since it is unreliable that mechanisms of both reactions were essentially different; these two points will be the object of further work.
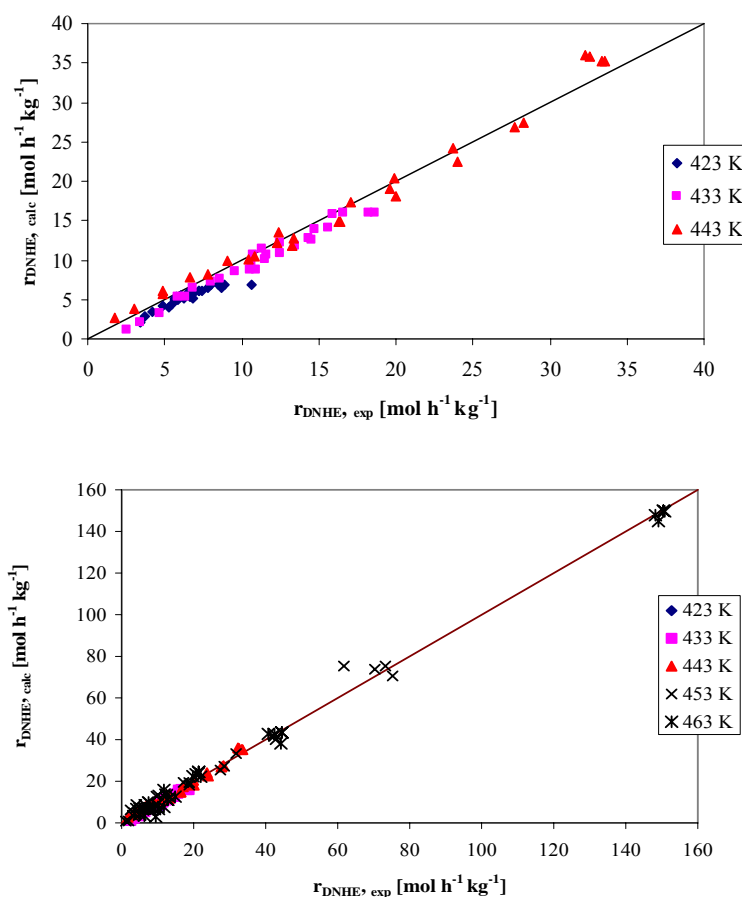


Fig. 12. Predicted by equation 7 versus experimental rate. Temperature range 423-463 K (up). Temperature range 423-443 K (down)

## 4. Conclusions

The thermally stable resin Amberlyst 70 has proven to be a good catalyst to obtain di-n-hexyl ether. Experiments performed in the absence of mass transfer effects show that DNHE yield on Amberlyst 70 is of the same order as DNPE, when the reaction is performed on the same set-up and experimental conditions. However, the reaction of DNHE synthesis is a bit more active but less selective. A kinetic model based on an Eley-Rideal mechanism has been proposed. A molecule of 1-hexanol from the liquid medium reacts with one adsorbed 1-hexanol molecule at the catalyst surface; the ether formed being released directly to the liquid phase. Surface reaction is considered as the rate-limiting step. Activation energy was computed to be 130 kJ/mol. Such kinetic

model needs to be improved by determining experimentally the chemical equilibrium constant.

## 5. Acknowledgments

## 6. Nomenclature
$a_j$ = activity of compound j
$d_p$ = particle diameter (μm)
$d_{pore}$ = pore diameter (nm)
$E_a$ = activation energy (kJ/mol)
$\varDelta H_j$ = adsorption enthalpy of compound j (kJ mol$^{-1}$)
$\hat{k}$ = intrinsic rate constant (mol h$^{-1}$ g$^{-1}$)
$K_j$ = adsorption equilibrium constant of j
$K_{eq}$ = thermodynamic equilibrium constant
$n_{H,0}$ = moles of 1-hexanol charged to the reactor
$n_{DNHE}$ = number DNHE moles
$N$ = stirring speed (rpm)
$r_{DNHE}$ = reaction rate of DNHE synthesis (mol h$^{-1}$ kg$^{-1}$)
$r^0_{DNHE}$ = initial reaction rate of DNHE synthesis (mol h$^{-1}$ kg$^{-1}$)
$R$ = gas constant (J mol$^{-1}$ K$^{-1}$)
$\varDelta S_j$ = adsorption entropy of compound j (J mol$^{-1}$K$^{-1}$)
$S_{DNHE}$ = selectivity to DNHE (%)
$S_g$ = surface area (m$^2$ g$^{-1}$)
$t$ = time (h)
$T$ = temperature (K)
$V_g$ = pore volume (cm$^3$ g$^{-1}$)
$V_{sp}$ = specific volume of the swollen polymer phase (cm$^3$ g$^{-1}$)
$W$ = weight of dry catalyst (g)
$X_H = X_{HeOH}$ = conversion of 1-hexanol (%)
$Y_{DNHE}$ = DNHE yield

*Greek letters*
$\rho_s$ = skeletal density (g/cm$^3$)
$\theta$ = porosity

*Subscripts*
D = DNHE, di-n-hexyl ether
H = 1-hexanol
W = water

## 7. References

Bringué, R., Tejero, J., Iborra, M., Izquierdo, J.F., Fité C. Cunill. F., (2006) *Journal of Catalysis* 244, 33-42.

Collin, J.R., Ramprasad. D., *European Patent Application EP 1 479 665* (2004).

Douaud, A., (1995) *Hydrocarbon Processing,*. <u>74</u>(2), 55.

Giavazzi, F., Terna, D., Patrini, D., Ancillotti, F., Pecci, G.C., Trerè, R., Benelli, M., (1991) *IX International Symposium on Alcohol Fuels*, vol. 1, p. 327.

Hagen, J., *Industrial Catalysis: a Practical Approach,* WILEY-VCH. (1999).

Jerabek, K., (1996) *ACS Symp. Series.* 635, 211-20.

Karpov, N.O., Bistroya, R.M. Fedoysuk, L.G., (1967) *Zh. Prikl. Khim.* 40, 219

Olah, O.A. *Us Patent 5.520.710* (1996)

Olah, G.A., Shamma, T., Surya Prakash, G.K., (1997) *Catal. Lett*. 46, 1-4.

Patrini, R., Marchionna, M. *UK Patent Application GB 2.323.844 A* (1998).

Pecci, G.C., Clerici, M.G., Giavazzi, M.G., Ancillotti, F., Marchionna, M., Patrini, R., (1991) *X International Symposium on Alcohol Fuels*, vol. 1, p. 321

Swistak, E., Mastagli, P., (1954) *Comptes Rend.* 239, 709-11

Tejero, J., Cunill, F., Iborra, M., Izquierdo, J.F., Fité, C., (2002) *J. Mol. Catal. A Chem.* 182–183, 541-54.

Van Heerden, J., Botha, J.J, Roets, P.N.J. (1998) *XII International Symposium on Alcohol Fuels, vol. 1*, Tsinghua Univ. Press, Beijing, p. 188.

Wittig, R., Lohmann, J., (2003) *Ind. Eng. Chem. Res*. 42, 183.