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Single stage synthesis of diisopropyl ether – an alternative octane enhancer for lead-free petrol

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Abstract

The title ether was synthesised using a single-pass trickle-bed reactor, over the ion-exchange resin catalyst Amberlyst 15, between 80°C and 140°C and 1 and 70 bar from a feed of propylene and water. Varying contact time experiments showed isopropanol to be the primary product in the reaction and diisopropyl ether the secondary product. In both the liquid and vapour phase, diisopropyl ether is formed by one of the two parallel, competing reactions: from the etherification reaction of isopropanol with propylene or from the dehydrative etherification of isopropanol. Apparent activation energies of 92 and 75 kJ mol^{-1} were measured for the hydration and etherification reactions, respectively. A linear dependence of rate on pressure was found. The Peng-Robinson–Stryjek-Vera equation of state together with the Wong–Sandler mixing rule was used to model the vapour–liquid behaviour of the system. For highest yield, diisopropyl ether synthesis should take place at high pressure and sufficiently high temperature to overcome the kinetic limitations.

Keywords: Diisopropyl ether; Isopropanol; Hydration; Etherification

1. Introduction

The introduction of the catalytic converter to reduce CO, NO_x and hydrocarbon exhaust emissions coupled with exhaust gas control legislation such as the 1990 Amendments to the US Clean Air Act of 1970 mandated fundamental changes in automobile fuels in Europe and North America. These changes restricted the use of heavy metal based octane enhancers such as tetraethyl lead, lowered permissible levels of light hydrocarbons and benzene in the fuel and raised the minimum fuel oxygenate content. This has led to substantial interest in alcohols and ethers which can both raise the oxygenate content of fuel and increase the octane number. C_1 to C_3 alcohols, whilst having higher octane numbers and being less expensive than ethers, have the disadvantage that they have a significantly higher blending Reid vapour pressure and are very water soluble. As a result, since 1990 the oxygenate of choice has been methyl *tert*-butyl ether (MTBE), though recent process improvements have allowed other ethers such as ethyl *tert*-butyl ether (ETBE) and tertiary amyl methyl ether (TAME) to compete economically.

All the current industrially significant octane enhancing ethers are based on the etherification reaction of C_1 to C_3 alcohols with C_4 or C_5 tertiary olefins. The primary refinery source of these olefins is the FCC unit, and while it is possible to increase the amount of

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Table 1
Properties of common blending alcohols and ethers [2–6]

Property	DIPE	MTBE	ETBE	TAME	Ethanol	Methanol
Average octane no.	105	109	110	105	114	120
Blending RVP[a] (psi)	4	8	4	2	18	>60
Oxygen (mass%)	16	18	16	16	35	50
Water solubility	Low	Low	Low	Low	High	High

[a] Blending Reid vapour pressure.

C_4 to C_5 olefins produced by changing operating conditions and using a different catalyst, it is considered unlikely that the demand for these olefins, for etherification needs, will be met in the near future. Consequently, interest is increasingly turning to the conversion of even heavier olefins to ethers [1]. However, if one considers that propylene constitutes the largest light olefin fraction produced in an FCC unit and that currently almost half of all propylene enters the petroleum pool as either propylene alkylate or polygasoline anyhow [2], one should also consider the option of using propylene for etherification purposes by producing diisopropyl ether (DIPE).

In spite of the significant attention being paid to the other ethers, there is scant information pertaining to DIPE. What little is available, is almost exclusively confined to the patent literature. Information available in the open literature relates mostly to its blending behaviour or the production economics [2–5]. Table 1 compares the blending properties of the common octane enhancing oxygenates with DIPE. The ethers all have very similar properties: DIPE has a poorer octane number, but a favourable blending Reid vapour pressure. Also, the driveability and combustion performance of DIPE has been shown to be the same as that of the other ethers [5]. What distinguishes DIPE from the other ethers is that it can be produced simply from the base olefin, propylene, and water. This eliminates the need for the refiner to obtain alcohol (methanol or ethanol), which may be subject to external price fluctuations, and frees him from the foreseen supply shortages of C_4 and C_5 tertiary olefins, since propylene is abundant. In comparison to the ethers, the primary blending alcohols ethanol and methanol have the significant disadvantages of high water solubility and a high blending Reid vapour pressure, though they compete favourably on the basis of octane number and relative oxygen content.

Presently DIPE is only obtained commercially as a by-product of IPA manufacture, and to the authors' knowledge, no industrial scale commercial plants have thus far been commissioned. Various patents, however, now propose the large-scale manufacture of DIPE from propylene and water in a two-stage process [2,7], a one-stage process [5] or by reactive distillation [8]. Alternatively, Texaco [9] offer a two-stage process using acetone and hydrogen as feedstocks. In all these processes DIPE is ultimately believed to be produced via the intermediate IPA. The reactions occurring in the system are thought to be:

$$C_3H_6 + H_2O \Leftrightarrow C_3H_7OH \quad \text{(IPA)} \qquad (1a)$$

$$C_3H_6O + H_2 \Leftrightarrow C_3H_7OH \qquad (1b)$$

$$C_3H_7OH + C_3H_6 \Leftrightarrow C_3H_7OC_3H_7 \quad \text{(DIPE)} \qquad (2a)$$

$$C_3H_7OH + C_3H_7OH \Leftrightarrow C_3H_7OC_3H_7 + H_2O \qquad (2b)$$

$$C_3H_6 + C_3H_6 \overset{+C_3H_6}{\Leftrightarrow} C_6H_{12} \overset{+C_3H_6}{\Leftrightarrow} C_9H_{15} \overset{+C_3H_6}{\Leftrightarrow} \cdots \qquad (3)$$

In the first two reactions, the intermediate IPA is formed either by the conventional route of propylene hydration (reaction (1a)) or, as is the case with the Texaco [9] patent, by acetone hydrogenation (reaction (1b)). IPA then reacts further in either one of these two reactions by etherification with propylene (reaction (2a)) or by dehydrative etherification (reaction (2b)). Which of the two ether formation reactions predominates, or if both occur, is not known. As is the case with the other ethers, a possible, undesired side-reaction is the formation of oligomers of the olefin [10,11], reaction (3). The hydration [11,12], etherification [13,14] and oligomerisation [15] reactions are all acid catalysed reactions, following a carbenium ion mechanism.

Initially, strong mineral acids such as sulphuric acid [10,16] were used to catalyse hydration and etherification reactions. Due to the inherent corrosion and separation problems, though strong solid acids have since replaced mineral acids. Presently, acidic ion-exchange resins are the catalysts of choice for both hydration [11,17,18] and etherification reactions [13,19,20]. Amongst the ion-exchange resin catalysts the most widely used is Amberlyst 15, manufactured by Rohm and Haas.

Almost all authors who have studied the reaction conditions for etherification reactions have done so at atmospheric pressure. Typically, MTBE, ETBE and TAME are all produced in a liquid phase, fixed-bed reactor system where pressure should have no effect on the reactions. Predictably, Rihko and Krause [21] found that pressure had no effect on the rate of TAME formation from methanol and isobutylene. On the other hand, for a high yield and rapid reaction, hydration reactions require the pressure to be elevated. Hydration reactions are typically carried out at pressures between 10 and 100 bar [10,11,18,22]. In hydration reactions, pressure influences the solubility of the olefin in the aqueous phase – the higher the pressure the higher the rate [10,11]. When using ion-exchange resins as catalysts, etherification reactions are carried out at temperatures between 30°C and 80°C [13,19,20]. Isopropanol manufacture is carried out above the critical temperature of propylene; hydration usually takes place between 100°C and 140°C [10,11].

The present paper describes the study of the single-stage production of DIPE over a commercial acidic ion-exchange resin, Amberlyst 15, where both the hydration and subsequent etherification reactions are performed within one catalyst bed. The reaction pathway as well as the effects of pressure and temperature are described.

2. Experimental

2.1. Materials

Propylene, 99.8% pure, was obtained from SASOL (Sasolburg, South Africa) and methane, likewise 99.8% pure, was obtained from Fedgas (Cape Town, South Africa). Both were used without any further purification. The liquid reagents IPA and DIPE, 99.7% and 99.0% pure, respectively, were supplied by Centrolab (Cape Town, South Africa). De-ionised water used in the study had a resistivity greater than 18 $\mathrm{M\Omega\,cm^{-1}}$. The commercial sulphonic acid ion-exchange resin, Amberlyst 15 (Rohm and Haas), used as the catalyst, was supplied in the dry hydrogen form.

2.2. Apparatus

The reactor configuration used for the experimental work is shown in Fig. 1. Liquid reagents (either pure water, IPA and DIPE, or mixtures thereof) were fed to the reactor by a high pressure liquid chromatography pump (1) (Hewlett-Packard Series 1100 Isocratic Pump) from a container (2) placed 1.5 m higher than the pump to prevent vapour lock. A scale (3) was used to determine accurately and independently the amount of liquid dispensed by the pump. Propylene from a pressurised gas bottle (4) was fed to the rig by a diaphram pump (5) (LEWA FC1). The pump head was cooled to -3°C by an ethylene glycol/water mixture, likewise to prevent vapour lock. The propylene and liquid feed streams were fed through heated lines to a combined mixer and preheater (9), filled with 1 mm glass beads, situated directly ahead of the downflow reactor (10). The reactor was a 330 mm long, 23 mm ID stainless steel tube with a 1/8 in. thermowell in the centre, whereby the axial temperature could be measured at varying bed heights. After the back pressure regulator (12) products flowed through another mixer (13), where the internal standard (methane) was introduced. The methane was used to determine the overall carbon balance for each experiment. The internal standard flow was controlled by a Brooks 5850TR mass flow controller (14). From the mixer, the gas phase reactor effluent flowed via a heated line (130°C), at atmospheric pressure, through a 300 μl GC sample valve (15). Finally, the stream flowed into a condensor (16), held at ~5°C, where the liquid components were trapped.

2.3. Analysis

Three hundred μl vapour samples were injected on-line into a Varian Model 3700 GC with an FID and a 50 m long, 0.25 mm diameter Hewlett-Packard HP1 (cross-linked methyl silicone gum) capillary column. This allowed quantitative analysis of propylene, the reaction products IPA and DIPE, as well as of the internal standard, methane. Water data were calcu-

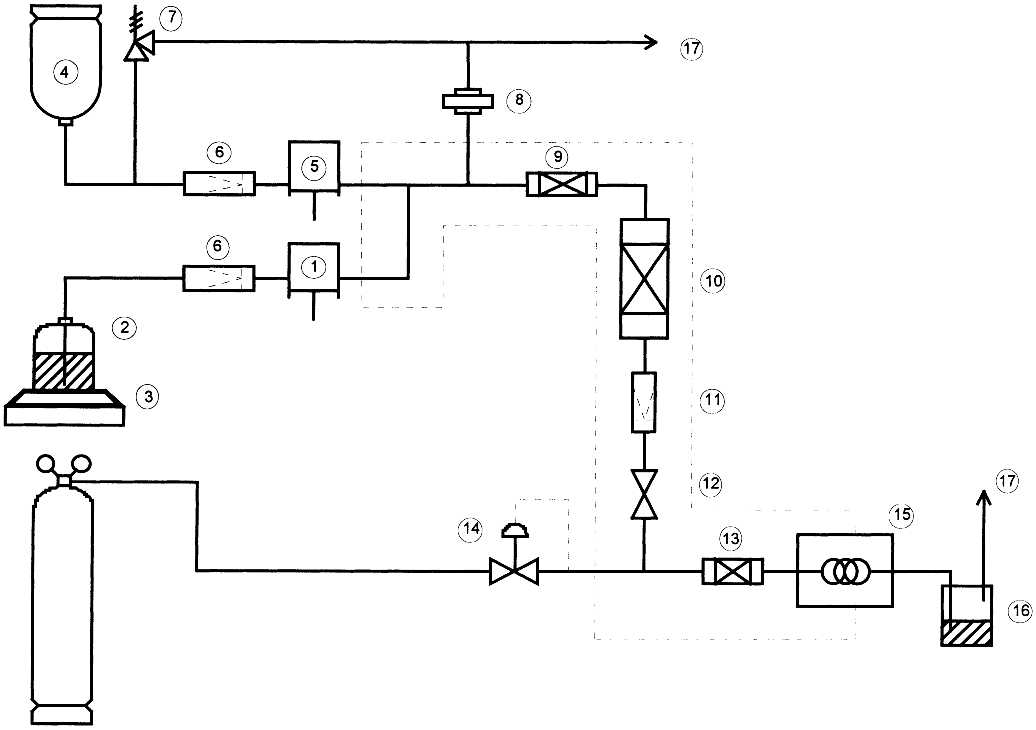

Fig. 1. Reactor configuration. Key: (1) pump, (2) liquid feed tank, (3) scale, (4) propylene tank, (5) propylene pump, (6) 0.5 μm filter, (7) pressure relief valve, (8) bursting disc, (9) mixer and preheat, (10) trickle-bed reactor, (11) 2 mm filter, (12) back pressure regulator, (13) mixer, (14) mass flow controller, (15) sample valve and gas chromatograph, (16) condensor, and (17) vent. Heated region enclosed by dotted line.

lated from the chromatographic results by mass balance. Integral analysis of the steady-state liquid product was performed by manual injection of samples into a Varian 1400 GC with a TCD fitted with a 1.8 m, 1/8 in., packed, 0.1% SP1000 Carbopack C column. This enabled analysis of water, IPA and DIPE, to be cross-correlated with the FID results.

2.4. Procedure

Before being loaded into the reactor, the resin was washed with benzene and then with methanol to remove any monomer remaining in the pores. It was then washed repeatedly with de-ionised water to remove all methanol and to swell the resin fully. The wet resin was loaded into the reactor. No dilution of the resin with inert solids was necessary as the reaction rate was sufficiently low so that the temperature could be kept constant to within ±1°C over the entire catalyst bed.

Prior to an experiment, the catalyst bed was flooded, at room temperature, by a high flowrate of the liquid feed to be used for the run. This leads to a thorough wetting of the catalyst bed which results in improved liquid flow distribution and mass transfer [23]. After wetting the resin, the propylene pump was switched on and the temperature slowly ramped (30–50°C h^{-1}) to approach the desired reaction temperature. Once the temperature had stabilised, on-line GC samples were taken every 15 min until the reaction was judged to have reached steady state (±3 h). An hour after this, the liquid trapped thus far in the condensor was drained so that the steady-state liquid sample could be collected. After a further 2 h running, during which analyses were performed every 15 min, the experimental run was stopped. The mass of liquid fed, the temperature and the pressure within the reactor were monitored throughout the run. The mass of propylene fed was determined by weighing the gas bottle before and after each run. Typical experimental conditions

Table 2
Typical experimental conditions

Catalyst mass, dry (g)	3–25
Particle diameters, dry (μm)	650–950
Reactor temperature (°C)	80–140
Reactor pressure (bar, absolute)	1.01–70
MHSV ($\mathrm{Mol_{feed}\,g_{cat}^{-1}\,h^{-1}}$)	3.0×10^{-4}–0.24
Acid site density (meq $\mathrm{g^{-1}}$)	0–4.7

are shown in Table 2. At these conditions the reactant mixture was two-phase: a super-critical propylene phase and a liquid phase containing water, IPA and DIPE, surrounding the catalyst particles. The reactor was thus a downflow trickle-bed. Even though it is thermodynamically possible for the compounds to form one gaseous and two liquid phases, at no stage in the reaction work was this ever observed, in either the reactor feed or effluent.

For this study, the overall propylene:water ratio was fixed at the molar stoichiometric ratio for DIPE formation of 2:1. Blank runs were performed which showed that all reaction was due to the catalyst. After every 3–4 runs, a repeat run was performed to check the catalyst activity and to ensure that previous results were not affected by deactivation. Data obtained from the rig was accurate to ±5% and consequently all runs in which the carbon balances were less than 95% or more than 105% were repeated. The relative standard deviation between successive steady-state GC traces was less than 2%.

3. Results

The four component vapour–liquid system was modelled using the Peng-Robinson–Stryjek-Vera equation of state [24] with the Wong–Sandler mixing rule [25]. The mixing parameters for the six binary mixtures were obtained from regression of literature experimental data. For five of the six systems, the experimental data could be correlated with an accuracy better than ±3% over the entire temperature and pressure range considered in this study. The propylene–water system, however, could only be correlated with an accuracy of ±7%, due to greater mixing non-idealities. Though no multi-component data were found in literature for this system, the fit for multi-component systems should be at least as good, or better, due to the dilution effect of mixing [26].

Combined chemical and phase equilibrium in a DIPE system with only hydration and etherification and an overall propylene to water ratio of 2:1 was predicted using the above-mentioned vapour–liquid model (Fig. 2). For a high yield, the system must clearly operate at high pressure, and preferably, at low temperature. A satisfactory hydration and etherification velocity can, however, only be achieved at elevated temperatures. For the majority of the present studies a temperature of 120°C and a pressure of 50 bar were chosen. The reactor thus operated as a trickle-bed.

A series of experiments at 120°C, 50 bar, a 2:1 propylene:water feed ratio and with varying contact time was performed to determine the initial reaction pathway (Fig. 3). Under these conditions the system consists of a liquid phase and a super-critical propylene phase. No catalyst deactivation was observed during the course of the experiments over a period of three months. Clearly, IPA is the primary product resulting from the hydration of propylene and DIPE the final, secondary product. No by-products, i.e. dimers or trimers of propylene, were produced at any stage, presumably due to water inhibition of the oligomerisation reaction. The inhibition effect of water has also been observed by other authors in studies on hydration and etherification reactions [10,11,27]. The data do not conclusively indicate which of the two possible DIPE formation reactions takes place.

A second series of high pressure contact time experiments at 120°C and 50 bar, this time only feeding IPA, was performed to see if the pathway of DIPE formation could be determined (Fig. 4). Under these conditions the system should be entirely liquid phase. The non-zero initial rates of formation of propylene, water and DIPE indicate that they are all primary products. Water and propylene are presumably formed directly from the dehydration of isopropanol. Via a primary pathway, DIPE can only form from the bimolecular dehydration of IPA. This is supported by the observation that the water concentration increased more quickly initially than that of propylene. The concentration of propylene passed through a maximum and then decreased. Over the same time interval the concentration of DIPE

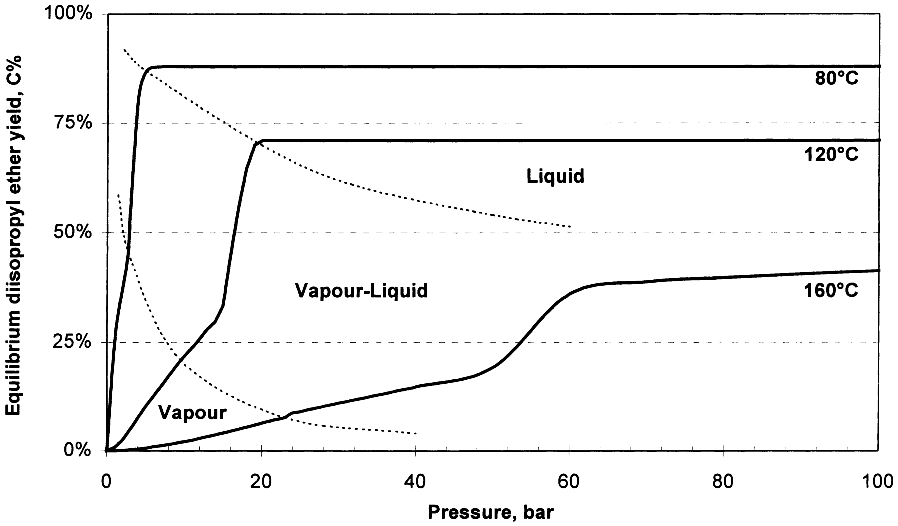

Fig. 2. Chemical and phase equilibrium in the DIPE system with an overall propylene to water ratio of 2:1. Only hydration and etherification reactions were considered.

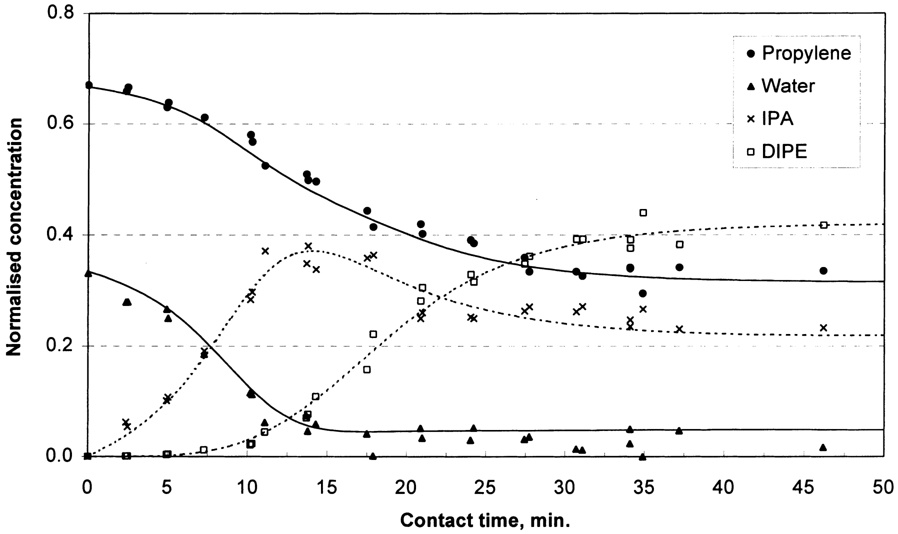

Fig. 3. Effect of contact time on approach to chemical equilibrium. 120°C, 50 bar, initial propylene:water ratio 2:1, 0.05 $\mathrm{mol_{feed}\,g_{cat}^{-1}\,h^{-1}}$.

appeared to increase progressively. This indicated that a secondary reaction was occurring which consumed propylene and formed DIPE via etherification of the olefin with the alcohol. Under liquid phase conditions, DIPE is thus formed either by etherification of propylene with isopropanol or by the bimolecular dehydration of isopropanol.

Starting from a feed of pure IPA, at 120°C, one can show that the same reactions occur in the vapour phase at atmospheric pressure as in the liquid phase at high pressure (see Fig. 5). Once again, water, propylene and DIPE are primary products formed from the reverse hydration and bimolecular dehydration reactions, respectively. A secondary reaction occurs,

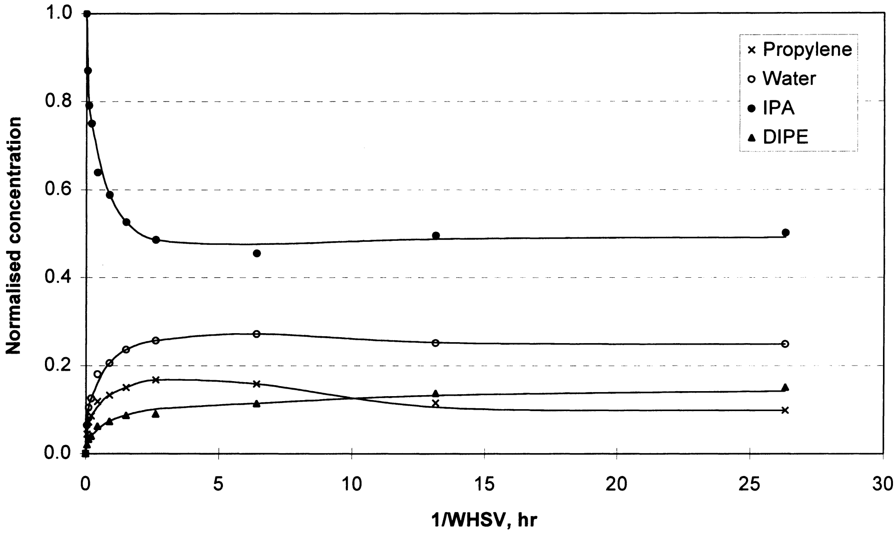

Fig. 4. Effect of contact time on approach to chemical equilibrium. 120°C, 50 bar, pure IPA feed, liquid phase.

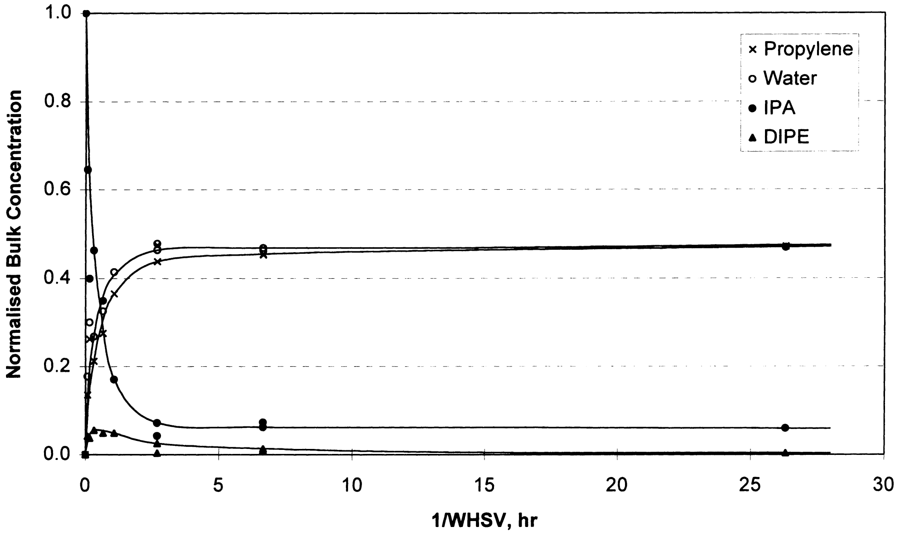

Fig. 5. Effect of contact time on approach to chemical equilibrium. 120°C, 1.01 bar, pure IPA feed, vapour phase.

which this time consumes DIPE. This can only be the reverse etherification reaction, forming propylene and isopropanol.

The contact time data have shown that only three reactions occur in the DIPE system over Amberlyst 15, and that these same reactions, depending on pressure, occur in both the vapour as well as the liquid phase. These three reactions are shown in the cyclic pathway in Fig. 6. DIPE is formed either from the bimolecular dehydration of isopropanol (reaction (3)) or by the etherification of propylene with IPA (reaction (2)). Clearly, IPA is formed from the hydration of propylene (reaction (1)).

Experiments conducted at 50 bar, 0.05 $\mathrm{mol_{feed}}$ $\mathrm{g_{cat}^{-1}\,h^{-1}}$ and a propylene to water ratio of 2:1, or an IPA to propylene ratio of 1:1 between temperatures of

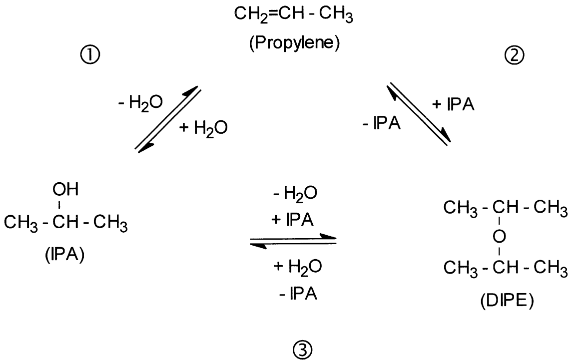

Fig. 6. Cyclic DIPE formation pathway.

80°C and 140°C showed, as is usual for almost all reactions, the log of the rate of formation of IPA and DIPE to be linearly dependent on the reciprocal of temperature, over the entire range. Apparent activation energies calculated from these experiments agree with those found by other authors who have studied hydration and etherification reactions over other ion-exchange resin catalysts [11,28,29]. The hydration reaction was found to have an apparent activation energy of 92±3 kJ mol^{-1}, the etherification one of 75±3 kJ mol^{-1}.

The influence of system pressure was investigated at a temperature of 120°C and 0.05 $mol_{feed}\ g_{cat}^{-1}\ h^{-1}$ over the pressure range 15–70 bar. To investigate the effect of IPA formation, propylene and water were fed in a 2:1 molar ratio, while for DIPE formation, IPA and propylene were fed in a 1:1 molar ratio. It was found that the rate of formation for both IPA and DIPE increased linearly with pressure (Fig. 7). This is due to a solubility effect. At the conditions under consideration the propylene concentration in the liquid phase, which surrounds the catalyst particles, increases linearly with pressure [30]. Consequently the rate of formation of IPA and DIPE also increases linearly.

The initial rate of IPA formation over Amberlyst 15 is comparable to literature data at both low and high pressure [11,31]. The rate of formation of diisopropyl ether on the other hand is an order of magnitude lower than the corresponding rate of formation of other ethers. At a 1:1 ratio of alcohol to olefin Tejero et al. [32] report initial rates of MTBE formation over Amberlyst 15 of 1.9×10^{-5} mol $g_{cat}^{-1}\ s^{-1}$. At identical conditions, the initial rate of formation of DIPE in the present study is 6.3×10^{-7} mol $g_{cat}^{-1}\ s^{-1}$, a factor of 30 slower. This large difference in the rates of formation likely results from a combination of two factors: firstly, the secondary propyl carbocation is significantly less stable than the tertiary isobutyl carbocation in MTBE synthesis, and secondly, water chemisorbs strongly on the catalyst, inhibiting propylene adsorption and subsequent reactions.

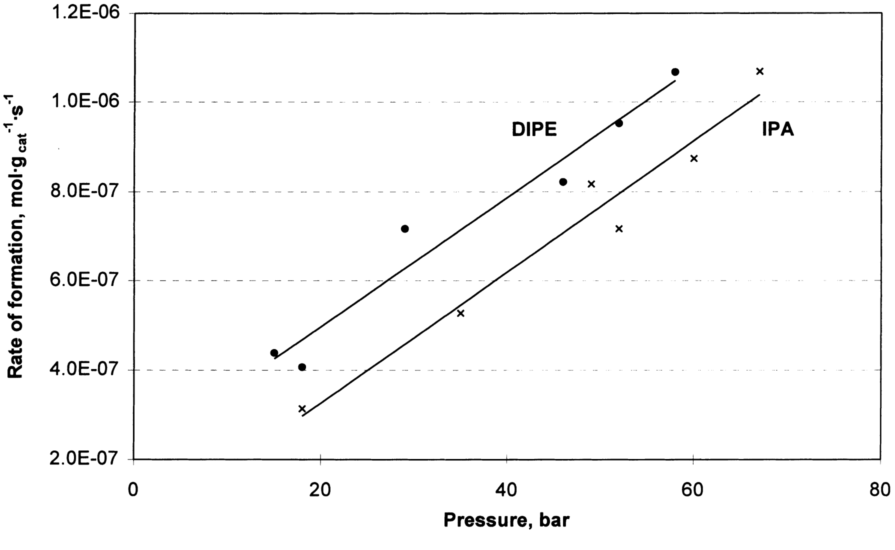

Fig. 7. Effect of pressure on the rate of IPA and DIPE formation. 120°C, 2:1 propylene to water ratio or 1:1 IPA to propylene ratio, 0.05 $mol_{feed}\ g_{cat}^{-1}\ h^{-1}$, conversion<15%.

4. Conclusions

DIPE is best synthesised at high pressure and a temperature high enough to overcome the retardation of the hydration and etherification rates caused by competitive chemisorption and the low stability of the secondary propyl carbocation. The ion-exchange catalyst, Amberlyst 15, has proven to be an efficient catalyst, showing negligible deactivation and high selectivity to the hydration and etherification reactions. No oligomeric by-products of propylene were produced. This allows any unreacted propylene, water and IPA in the reactor effluent to be recycled to extinction.

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References

[1] J. Ignatius, H. Järvelin, P. Lindqvist, Hydrocarbon Processing 2 (1995) 51–53.

[2] T.L. Marker, H.U. Hammershaimb, R. Marinangeli, W.H. Keesom, U.G. Bozzano, AIChE Annual Meeting, 1993.

[3] Oil & Gas J. 5 (25) (1992) 39-41.

[4] H.U. Hammershaimb, U.G. Bozzano, W.H. Keesom, T.L. Marker, Fuel Reformulation 5 (1993) 36–42.

[5] T.L. Marker, W.H. Keesom, R. Schmidt, S. Davis, R. Marinangeli, Conference on Clean Air Act and Reformulated Gasolines, 1994.

[6] H.L. Brockwell, P.R. Sarathy, R. Trotta, Hydrocarbon Processing 9 (1991) 133–141.

[7] J.E. Child, B.C. Choi, F.P. Ragonese, US Patent 4 935 552, 1990.

[8] T.L. Marker, G.A. Funk, H.U. Hammershaimb, US Patent 5 504 258, 1996.

[9] R.J. Taylor, Jr., P.E. Dai, J.F. Knifton, US Patent 5 583 266, 1996.

[10] W. Neier, J. Woellner, CHEMTECH 2 (1973) 95–99.

[11] L. Petrus, R.W. De Roo, E.J. Stamhuis, G.E.H. Joosten, Chem. Eng. Sci. 39(3) (1984) 443–446.

[12] J.N. Nowlan, T.T. Tidwell, Acc. Chem. Res. 10 (1977) 252–258.

[13] F. Ancillotti, M.M. Mauri, E. Pescarollo, J. Catal. 46 (1977) 49–57.

[14] E. Velo, L. Puigjaner, F. Recasens, Ind. Eng. Chem. Res. 27 (1988) 2224–2231.

[15] A.V. Sapre, F.J. Krambeck, Chemical Reactions in Complex Mixtures, Van Nostrand Reinhold, New York, 1991.

[16] A.M. Al-Jarallah, A.K.K. Lee, A.B. Siddiqui, Chem. Eng. J. 39 (1988) 169–174.

[17] R.L. Albright, I.J. Jakovac, Rohm and Haas, 1985.

[18] M.J. Gavaghan, C.J. Papile, Rohm and Haas, 1991.

[19] J. Tejero, F. Cunill, J.F. Izquierdo, Ind. Eng. Chem. Res. 28 (1989) 1269–1277.

[20] C. Fité, M. Iborra, J. Tejero, J.F. Izquierdo, F. Cunill, Ind. Eng. Chem. Res. 33 (1994) 581–591.

[21] L.K. Rihko, A.O.I. Krause, Ind. Eng. Chem. Res. 34 (1995) 1172–1180.

[22] Y. Izumi, Catal. Today 33(4) (1997) 371–409.

[23] L.B. Møller, C. Halken, J.A. Hansen, J. Bartholdy, Ind. Eng. Chem. Res. 35 (1996) 926–930.

[24] R. Stryjek, J.H. Vera, Can. J. Chem. Eng. 64 (1986) 334–340.

[25] D.S.H. Wong, S.I. Sandler, AIChE J. 38(5) (1992) 671–680.

[26] A. Wyczesany, Ind. Eng. Chem. Res. 33 (1994) 1971–1978.

[27] F. Cunill, M. Vila, J.F. Izquierdo, M. Iborra, J. Tejero, Ind. Eng. Chem. Res. 32 (1993) 564–569.

[28] A. Gicquel, B. Torck, J. Catal. 83 (1983) 9–18.

[29] A. Rehfinger, U. Hoffmann, Chem. Eng. Sci. 45(6) (1990) 1605–1617.

[30] C.C. Li, J.J. McKetta, J. Chem. Eng. Data 8 (1963) 2.

[31] J.H. Hiestand, Ph.D. Thesis, University of Michigan, 1961.

[32] J. Tejero, F. Cunill, J.F. Izquierdo, M. Iborra, C. Fité, D. Parra, Appl. Catal. A 134 (1996) 21–36.