TRANSALKYLATION OF DIISOPROPYLBENZENE WITH BENZENE IN SUPERCRITICAL CARBON DIOXIDE

J.L. Sotelo, L. Calvo*, D. Capilla, and A. Pérez-Velázquez
Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, SPAIN.
Phone: +34 91 394 4185   Fax: +34 91 394 4185   email: lcalvo@quim.ucm.es

ABSTRACT

This work was devoted to investigate the main variables affecting the production of cumene by transalkylation of diisopropylbenzene with benzene using supercritical carbon dioxide as solvent and a beta zeolite as catalyst. Pressure did not significantly affect process yield. On the contrary, temperature within the interval of 150-250ºC greatly increased reaction rate and catalyst stability. High contact times were also beneficial for enhancing product yield. The process in supercritical carbon dioxide was compared to liquid phase. The comparison was run at different temperatures and several contact times. At all conditions, catalyst activity was pretty similar in both media while the zeolite stability was lower in supercritical conditions. The analysis of the spent catalyst samples revealed a higher and more evolved coke content in the supercritical treated samples. The results were ascribed to the lower solvating capacity for heavy hydrocarbons of the supercritical medium.

INTRODUCTION

Monoalkylbenzenes such as isopropylbenzene (cumene, CUM) are important intermediates for the synthesis of large-scale chemical commodities. The synthesis of these compounds by benzene (B) isopropylation over acidic catalysts is usually accompanied by the formation of isomers such as diisopropylbenzene (DIPB). To improve process yield, dialkylates are then transformed to CUM by further reaction with benzene (transalkylation) in a separate reactor. Liquid-phase conditions are preferred since this implies slower catalyst activity decay and better selectivity to the desired product.

The use of supercritical (SC) CO_2-based reaction media for optimizing catalyst activity and selectivity in the transformation of alkylaromatics over porous catalysts has been widely investigated. Although there are clear advantages of supercritical fluids (SCFs) over gases for enhancing heterogeneous alkylation catalysis [1,2,3], it is not clear whether SCFs may perform better than liquid media. On the one hand, SCFs provide mass-transfer advantages over liquids, but the solubilities of heavy organics may be lower leading to changes in product selectivity or increased catalyst deactivation. For example, Ginosar et al. conducting the comparison of the alkylation of toluene with ethylene over USY and sulfated zirconia catalysts found that, deactivation rate increased as reaction conditions changed from liquid to supercritical for both catalysts [4].

On the contrary, Tian *et al*. demonstrated on the alkylation of benzene with propene over H-Beta zeolites that the supercritical reacting media was efficient to improve the reactivity and to prolong the catalyst life [1]. Similarly, Salinas *et al.,* investigating the solid-acid-catalyzed isobutene-butene alkylation reaction in supercritical isobutene, found that operation in the supercritical region resulted in higher conversions comparing to liquid-phase [5]. However,

the higher temperature applied to reach SC conditions could explain the enhancement of reactant conversions in these studies.

The aim of this research was to investigate the transalkylation of DIPB with B to produce CUM in supercritical carbon dioxide. In a previous work, the catalyst was screened among nine acidic commercial beta, Y and mordenite zeolites with different aluminium contents (e.g. Si/Al molar ratio) [6]. At the optimum Si/Al molar ratio, the three zeotypes gave high conversion in conjunction with high selectivity for the product of interest and were stable against pressure.

Because the batch conditions did not allow for direct evaluation of the catalyst aging, the investigation was continued in a continuous flow apparatus. This work describes the results after studying the most important parameters such as pressure, temperature, and contact time (W/F). The beta zeolite was chosen to conduct the investigation since it proved to be a long lifetime catalyst for the transalkylation of diethylbenzene with B in liquid phase [7]. Selected tests were carried out in conventional conditions (liquid phase) and SC conditions with CO_2, in order to establish the differences in activity and stability of the catalyst. The goal was to check the possible benefit of supercritical conditions on catalyst lifetime.

I- MATERIALS AND METHODS

Materials. The catalyst used was an H-β extruded zeolite with a Si/Al molar ratio of 13. The particle crystal size was in the 0.2-0.4 μm range, and the powder was granulated into particles of 32-65 mesh. The binder meant about 50% weight. The feedstock consisted on a mixture 1/2 mol% p/m-isomers of DIPB, corresponding to thermodynamic equilibrium at room temperature (Across Organics). This composition simulated the feed for an industrial transalkylation reactor. The molar ratio between B and DIPB was equal to 10. Supercritical tests were run with a CO_2 molar ratio of 10 to 1 with respect to the aromatics mixture.

Experimental apparatus. The catalytic tests were carried out in a continuous flow apparatus. The set up included five main parts: a CO_2 and an aromatics mixture feed lines, a preheater, a tubular reactor, a pressure regulating system and a product recovery section. The CO_2 was cooled to -15ºC in a thermostated bath and pumped with a head-cooled membrane pump (Milroyal D, Dosapro Milton Roy). The aromatics mixture was fed in by a similar pump. The preheater consisted of 316 ss coiled 1/8" tubing inserted in a heating jacket. The tubular reactor, made of 316 ss, had an internal diameter of 1.75 cm and a length equal to 30.5 cm. The temperature was controlled ± 2ºC by a heating jacket around it and was recorded by a thermocouple placed inside the reactor. The pressure was controlled in a needle valve pressure regulator system within ± 0.1 MPa. The effluent was quenched to ambient temperature through the use of a countercurrent heat exchanger. A series of three glass collectors immersed in a refrigerant solution at -10ºC helped to condensate the gas products.

Method. The liquid reactant mixture was kept in a vessel at ambient temperature under slight N_2 pressure and on top of a balance to control the feed consumption. Its composition was obtained by weight and controlled by GC analysis. The catalyst was loaded into the reactor and dried overnight at 250ºC. The experiment started after pumping the aromatic mixture. In supercritical tests, CO_2 was used as diluent. The products were recovered in the glass collectors at regular intervals and analyzed by GC.

Critical point and fluid properties determination. The critical parameters for 0% conversion were 73.6ºC and 122.5 bar. They did not significantly change during the course of the reaction since CUM and DIPB critical properties were similar and both compounds were

in very low proportion with respect to CO_2. Critical constants, equilibrium values and liquid and supercritical phases properties were calculated by the Predictive Redlich Kwong Soave (PSRK) equation of state using the Aspen Plus process simulation software (Aspen Technologies, Inc. Cambridge, MA).

Coke analysis. The spent catalyst was dried at 250ºC for 0.5 hours to eliminate water and volatile organic matter. Total coke content, including the light and heavy coke, was determined from the thermogravimetrical analysis, corresponding to the overall weight loss recorded from 250ºC to 700ºC. Elemental analysis was used to determine the carbon, hydrogen and nitrogen proportion. The ratio H/C gave an indication of aromatic and/or condensation degree of deposits.

Analytical procedures. A Varian CP 3800 Gas Chromatograph, equipped with a CP-Sil 5 column (15-m length x 0.32-mm ID) and a FID detector was used to quantify the products in liquid samples. Peaks were identified by retention time matching with known standards. Seven major byproducts were analyzed including toluene, ethylbenzene, n-propylbenzene, secbutylbenzene, m-diisopropylbenzene (m-DIPB), diphenylmethane and diphenylethane.

II-RESULTS AND DISCUSSION

The isomerization product, m-DIPB was found to be the major byproduct. Thus, product yield and selectivity were calculated taking only into account the transalkylation and isomerization products. Mass balances ranged from 92% to 100%. Average uncertainty in reported data was typically ± 5%. The results obtained while investigating the effect of operating variables and the type of solvent on catalyst activity and stability are discussed next.

Effect of pressure on cumene yield

The use of subcritical (gas) or supercritical conditions on the performance of the catalyst was evaluated at 180ºC and different contact times. The results of cumene yield are shown in Figure 1. In principle, increased pressure from gas to supercritical fluid values should lead to higher fluid densities, which would provide higher reactant concentration and minimal reduction in mass transfer properties, which in turn should lead to higher conversions. However, supercritical conditions, defined as an increase in pressure from 80 bar (gas phase) to 160 bar, did not enhance the catalytic activity at any W/F. Similar results were found in our preceding work in batch operation [6]. The increase in pressure from 80 to 130 bar did not affect the performance of any of the three zeotypes tested. The results were explained in terms of fluid properties. Since temperature was quite far from the critical point, the disparity in pressure from one condition to another was not enough to significantly affect solvent density or DIPB diffusion coefficient as shown in Table 1. However, Salinas *et al.* discovered a significant improvement in activity and catalyst lifetime when changing from subcritical to supercritical conditions for isobutene/butane alkylation over a beta zeolite (Si/Al =30) [5]. They also played with pressure in isothermal operation but around the critical point where density changes were large.

Effect of temperature and contact time on cumene yield

Usually, increased contact times help process yield. Nevertheless, temperature may affect DIPB conversion in different ways. On the one hand, an increase in temperature would have a positive effect on kinetic constant as defined by the transition state theory. However, high temperatures may promote side reactions, such as isomerization whose activation energy is

higher than that of transalkylation [7] or cracking and disproportionation reactions producing coke precursors that would reduce catalyst activity. On the other hand, high temperatures would decrease density and so solubility of reactants which can reduce rates for the transalkylation reaction. Therefore, the effect of temperature is not easy to predict. Temperatures ranging from 150 to 250ºC were explored at different contact times (3-36 min) and 130 bar. At 250ºC, equilibrium conversion was reached at all W/F as observed in Figure 1 a. At lower temperatures, high contact times were necessary to achieve equilibrium conversion. At 150ºC, maximum conversion was not even achieved at the highest W/F. Within the range of investigated conditions, the decrease in density was not significant (see Table 1), so the kinetic enhancement by high temperatures prevailed.
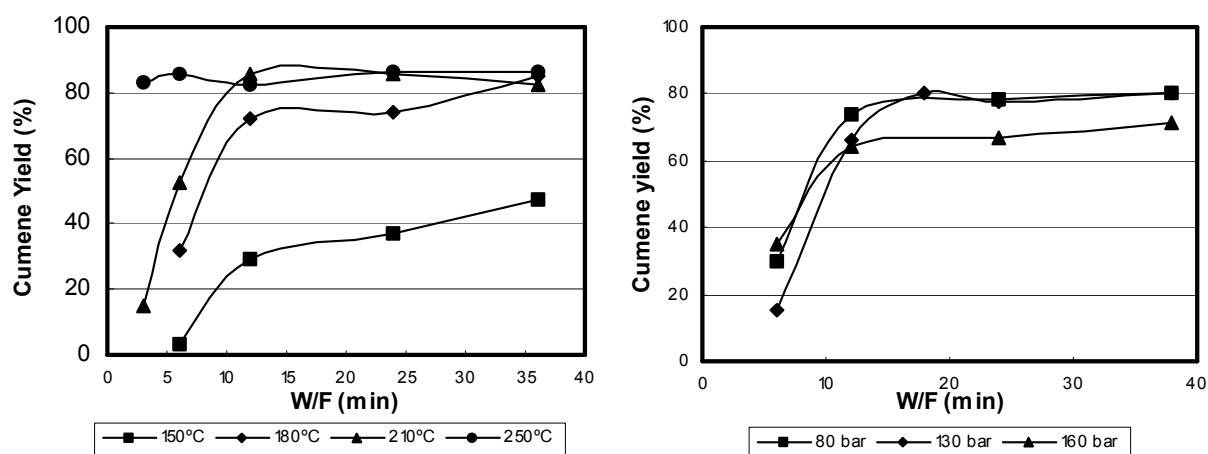

Figure 1. Effect of a) temperature and b) pressure on cumene yield.

Table 1. Density and DIPB diffusion coefficient of reaction fluid mixtures.

Supercritical conditions		
Conditions	ρ_{total} (g/cm^3)	D_{DIPB} (m^2/s)*10^7
Effect of temperature at 130 bar		
180ºC	0.2068	0.629
210ºC	0.1813	0.713
250ºC	0.1579	0.833
Effect of pressure at 180ºC		
80 bar	0.1185	1.023
130 bar	0.2068	0.629
160 bar	0.2616	0.511

Liquid phase, pressure =30 bar		
Temperature	ρ_{total} (g/cm^3)	D_{DIPB} (m^2/s)*10^7
180ºC	0.6199	0.0852
210ºC	0.5706	0.1132
250ºC	0.5138	0.1604

Effect of temperature on catalyst deactivation

Elevated temperatures also helped to keep the catalyst active for longer periods of time as demonstrated by the stability tests conducted between 180ºC and 250ºC at 32 min W/F (Figure 2). At 250 ºC, the decrease in the catalytic activity was only 8 % in 12 hours after the conversion started to decrease at 50 hour run. On the other hand, deactivation started at higher times on stream as temperature increased. This result is likely to be due to the high selectivity for the transalkylation reaction at those temperatures reducing the formation of cracking products responsible for the catalyst deactivation.
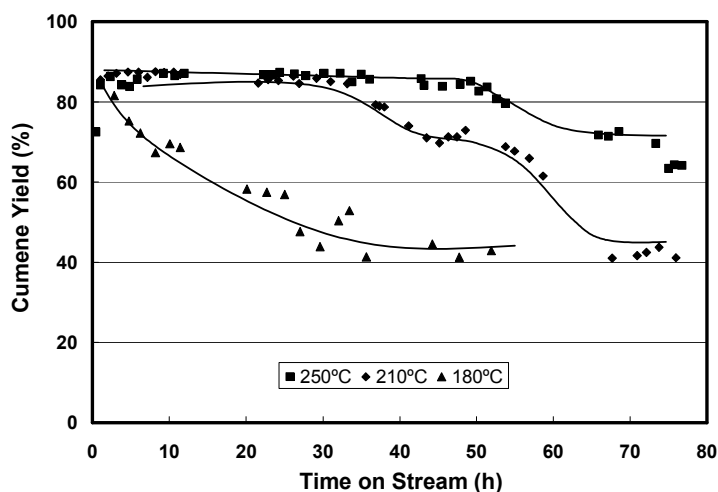
Figure 2. Effect of temperature on catalyst lifetime at W/F = 32 min.

Comparison between SC and conventional liquid phase conditions.

Our previous work investigating the performance of several zeolites demonstrated the increase in catalyst activity as reaction conditions changed from liquid to supercritical conditions even for the beta zeolite used in this work [6]. The results in continuous operation are plot in Figure 3a. At 210 ºC the catalyst showed an activity in liquid phase very similar to the one obtained in SC conditions. Although diffusion properties are improved at SC conditions, mass transfer did not probably limit the reaction rate in continuous operation since the contact between the catalyst and the mixture is more efficient. Nevertheless, the comparison of catalyst performance with operating time shown in Figure 3b demonstrated that the catalyst stability seemed to be lower at supercritical conditions, especially at 250ºC. At 210ºC, the catalyst deactivated fast in both media. Similar results were found on the alkylation of toluene with ethylene over USY and sulfated zirconia catalysts [5]. Catalyst lifetime was longer in liquid phase tests. A possible explanation is that at supercritical conditions, reaction mixture density is much lower, and so the solubility of heavy hydrocarbon which act as catalyst deactivating agents.
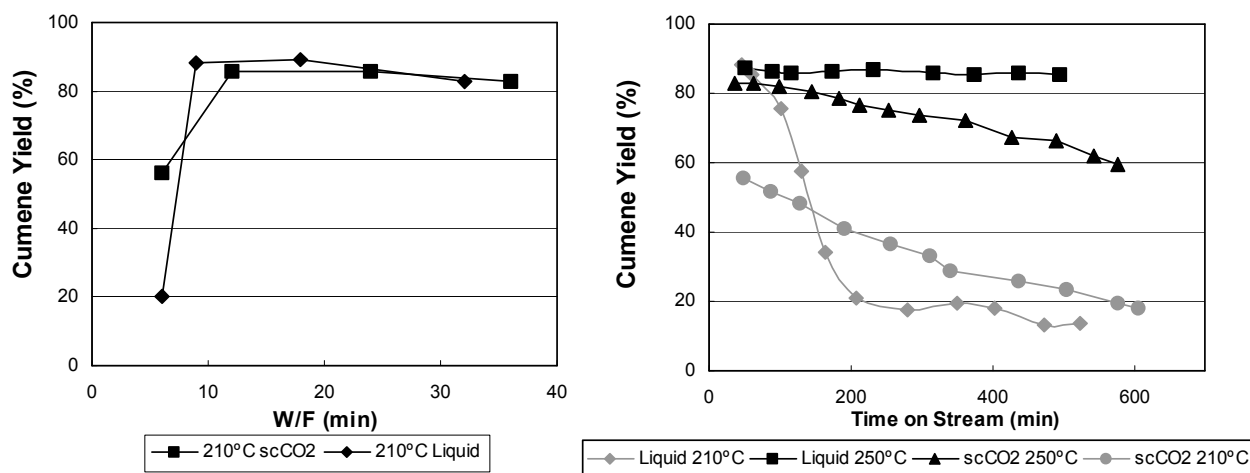

Figure 3. Comparison of a) catalyst activity and b) catalyst stability (W/F = 6 min) in supercritical CO_2 and liquid phase at different temperatures.

In fact, the analysis of the coke content on the spent catalysts shown in Table 2 revealed that on average, the amount of coke deposit was higher in supercritical than in liquid spent catalyst samples, even though the liquid-phase samples were on run for longer periods of time. On the other hand, the elemental analysis demonstrated that the hydrogen to carbon proportion was always higher than one indicating that the nature of the coke deposits was highly condensate [10]. The supercritical treatment seemed to slightly reduce this ratio that could be attributed to a more aromatic character of the coke.

Table 2. Total amount and elemental analysis of the coke deposits in spent catalysts obtained at different temperatures in supercritical and liquid phases.

Conditions	Time on Stream (h)	H/C	% Coke (250-700ºC)
SC-CO$_2$, 210ºC	7.5	1.75	16.6
SC-CO$_2$, 250ºC	5.0	2.26	12.0
Liquid, 210ºC	9.0	2.37	12.9
Liquid, 250ºC	10.0	2.24	11.7

CONCLUSION

This work demonstrated that transalkylation of DIPB with B could be carried out over a beta zeolite with high yields in supercritical carbon dioxide. However, the use of supercritical medium did not result in a better catalytic activity than the conventional practice at liquid phase. The process did not seem to be controlled by mass transfer so the higher diffusion coefficients of the supercritical medium were not advantageous. On the contrary, the lower density of this solvent compared to the liquid organic mixture was detrimental for solubilizing the coke precursors resulting in higher deactivation rate. On the other hand, high temperatures were required from kinetics, so it was necessary to operate far from the critical point where supercritical solvent properties greatly vary. At these conditions, pressure tuning was useless and the positive effect on kinetics prevailed over the slight decrease in density as temperature was raised. Therefore, it is important when evaluating the potential of the replacement of organic solvents for supercritical fluids in a particular application to analyze if the working conditions will allow exploiting the beneficial properties of these solvents.

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