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A one-step catalytic separation process for the production of cumene

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A novel reactor design has been completed and tested for catalytic separation and production of cumene. Use of a reactive separation column packed with a solid acid catalyst where simultaneous reaction and partial separation occur during cumene production allows separation of unreacted excess benzene from other products as they form. This high yielding system allows for one step processing of cumene, with reduced need for product purification. Beta catalysts produced promising results, including cumene selectivity for catalytic separation reactions starting at 85% and cumene reaction yield up to 30% at a reaction temperature of 115 °C. Simultaneously, up to 76% of unreacted benzene was separated from the products.

KEY WORDS: benzene alkylation; catalytic distillation; cumene; reactive separation.

1. Introduction

The alkylation of benzene with propylene is an important commercial alkylation reaction that produces cumene, a petrochemical feedstock produced in large quantities for use in the manufacture of phenol and acetone [1,2]. Conventionally, cumene is manufactured using $AlCl_3$ or phosphoric acid catalysts that create both equipment corrosion and environmental problems [3,4]. The difficulties arising from the conventional catalysts have spurred the use of more environmentally friendly solid acids such as zeolite-based catalysts [5–8]. No matter the catalyst used, conventional techniques require large excess amounts of benzene. Compounding matters, the reaction occurs with no simultaneous separation, which necessitates further multiple energy-intensive distillation steps including (1) separation of the product from the excess benzene, and (2) purification through separation of cumene from the by-products.

More recent technologies, such as catalytic or reactive distillation, achieve catalytic reaction and continuous separation of unreacted benzene and products by distillation in one step, in a single catalytic distillation reactor [9,10]. The advantage of using a solid-catalyzed reaction over a catalyst that acts as distillation packing inside the distillation column is more pronounced when used in reactions limited by equilibrium. While these systems still require cumene be separated from the reaction by-products, they contain an energy efficient distillation step of separating unreacted benzene from the products. However, these later technologies require the use of high pressures in the column to operate [9,11]. In contrast, our reactor system also allows reaction and partial separation in one single column, but with the more energy efficient process of ambient pressure. In our catalytic reactive separation system, by the application and removal of heat unreacted benzene is separated from the products as they form through the inherent difference in boiling points of reactants and products. No added pressure is necessary. This work is a preliminary study of the effect of the reactor configuration on the performance of the catalytic separation process under selected operating conditions. We have optimized this system through a series of catalysts and configuration studies, reported herein.

2. Experimental

2.1. Reactants and catalyst

The catalysts used were protonated (H^+) β-zeolite in powder form (Si/Al_2:25/1) and in pellets of 80% Beta-zeolite(Si/Al_2:24/1) and 20% alumina binder, purchased from Zeolyst International. Benzene (Aldrich, 99 + %) was used without further purification. The alkylating agent, propylene 14.3% in a balance of nitrogen, was purchased premixed from TriGas. Relative cumene yield was defined as the amount of cumene produced over the maximum amount of cumene calculated by stoichiometry. Cumene relative selectivity is the amount of cumene produced over the sum of all the products obtained. The experimental error was calculated as 6%.

Initial studies were conducted to determine reaction temperature and catalyst amounts. Though not optimized, the temperature of 115 °C was chosen as it is the intermediate temperature between the boiling points of

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benzene and cumene (80 °C and about 152 °C), and catalyst amounts of 200 mg for powder or 400 mg for pellets were chosen not only for the alkylation reaction to occur, but also for the separation of reactants and products.

2.2. *Reactor and process description*

The reactive separation system consists of a reactant delivery section, a vertical flow-through catalytic column, and a collection part with a reboiler and condenser, as presented in figure 1. The reactants are fed into the reactor by a mass flow controller that delivers 3.5 ccm of a gaseous mixture of 14.3% of propylene in nitrogen, and a syringe pump that injects 2.7 cc/h of liquid benzene. The system is kept at atmospheric pressure. The reactants are fed through two separate inlets, which could be located at the same level or at different points in the vertical column (configurations A, B, or C), as shown in figure 2. The vertical flow-through reactive column consists of a 3.5 in. or 6 in. stainless steel tube of 3/8 in. OD, in which the catalyst was packed and held by quartz glass wool and quartz beads, as shown in figure 3. Before beginning the reaction, the catalyst was pretreated by flowing 10 ccm of dry nitrogen through the column at around 115 °C for at least 30 min. Once the column was stable at the reaction temperature of 115 °C, the reactants were fed in to start the reaction. A flexible heating tape connected to a heater was wrapped around the reactive column to keep the reactor at the desired temperature.

A chilled water circulated glass condenser was attached to the top of the column to cool and condense unreacted benzene in a collection glass flask. A reboiler unit, composed of a collection glass bulb and a heating mantle connected to a heating controller, was attached to the bottom of the column to provide heat and collect cumene and heavier products. This reboiler unit was kept around 80 °C, the boiling point of benzene, in order to evaporate any unreacted benzene and send it back to the column. After 3 h of reaction time, the flow of reactants was stopped and the products collected at the top and bottom of the column. The final volume of the collected products of the alkylation reaction was taken to 25 ml using hexane. Then, the products were identified by mass spectroscopy using a GC/MS Hewlett Packard 5890 Series II Plus, and quantitatively analyzed by a Hewlett Packard 5890A gas chromatograph equipped with a capillary column Bentone 34/DNDP SCOT (0.02 in. × 50 ft, or 0.5 mm × 15.2 m) from Supelco and a flame ionization detector.

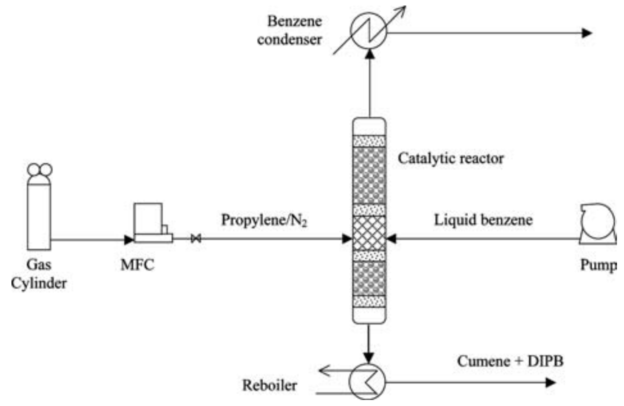

Figure 1. Process diagram (not to scale).

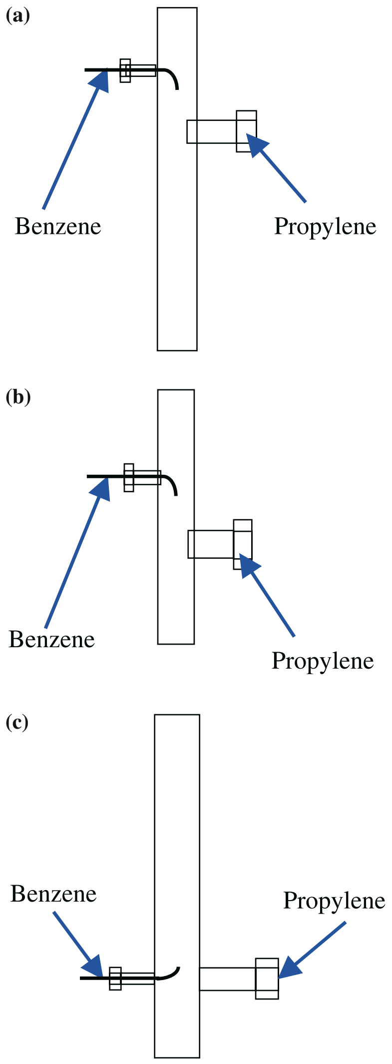

Figure 2. Reactor configurations: (a) Six-inch-long column with reactant feeding ports separated by 1 in., (b) 3.5 in. column with reactant feeding ports separated by 1 in., and (c) 6 in. column with reactant feeding ports located at the same height.

3. Results and discussion

The reactive separation column packed with a solid acid catalyst where both reaction and separation occur, allowed separation of unreacted excess benzene from the products as they formed. The reactants propylene and benzene met inside the reactive column in the presence of a solid catalyst at 1 atm. and 115 °C. As the benzene alkylation reaction proceeded, cumene was formed. At the same time, vapor benzene rose through the column and exited through the top of the tower, together with unreacted propylene, as the light stream; while produced liquid cumene, together with all the other by-products (mainly di-isopropylbenzenes, DIPB), dropped down the column and exited the bottom of the tower as the heavy stream. Ideally, all the unreacted benzene would escape to the top of the column, and all cumene formed would go to the bottom products.

Table 1 shows the results of the reactive separation of cumene formed by alkylation of benzene with propylene, using the catalyst in powder and pellet form in the different reactor configurations. As seen, in all the reactor configurations relative cumene selectivity with respect to products was above 85% for both powdered and pelletized catalysts, but the cumene reaction yield and separation of unreacted benzene and cumene formed varied greatly from one system to another. With configuration A, a very low cumene reaction yield occurred, and most of the cumene formed was taken to the bottom, as desired, but most of the unreacted benzene also collected at the bottom. The separation of unreacted benzene and produced cumene in the reactor with configuration B was not very good, as similar amounts of reactant and products were obtained in the amounts collected from both the top and bottom.

Of the different reactors tested, configuration C shown in figure 2(c) gave the best results in terms of reactant-product separation for both pelletized and powdered catalysts. When pellets were used, 76% of the unreacted benzene rose to the top of the column, but 24% of benzene dropped with the bottom products. With the cumene, 63% dropped to the bottom, but 37% of cumene rose to the top. For this reaction, relative cumene yield was about 30% and cumene selectivity was 90%. When powdered catalyst was used in reactor configuration C, 62% of the unreacted benzene rose to the top of the column, and 86% of the cumene formed in the reaction dropped with the bottom products. The cumene yield for this reaction was about 20% and the relative selectivity was 85%.

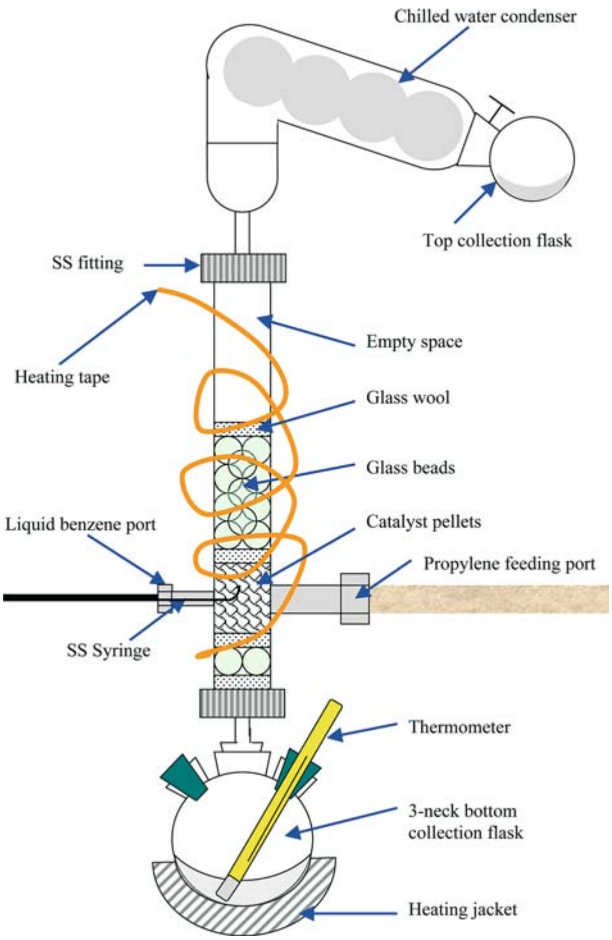

Figure 3. Detail of column set up for catalytic separation.

As seen, although our system does not have the high yield of the reactive distillation processes (above 98%), our system does not require the high operating pressures of the other processes [9,11,12] nor does it use a reflux system for the top products. While complete separation of unreacted benzene from the cumene formed is not possible in one pass, additional testing and design optimization should improve the separation results. Even in this preliminary stage, the selectivity obtained with our catalytic separation reactions stayed in the 85 percentile at the relatively low reaction temperature of

Table 1

Results of reactive separation of cumene, with reactor at 115 °C and 1 atm, feeding 3.5 ccm 14.5% propylene/N_2 and 2.7 ml liquid benzene, after 3 h reaction

Run	Catalyst	Reactor configuration	Rel. cumene selectivity %	Rel. cumene yield %	Benzene wt%		Cumene wt%	
					Top	Bottom	Top	Bottom
1	200 mg Powder	A	87	3	31	69	11	89
2	200 mg Powder	B	89	21	50	50	62	38
3	400 mg Pellets	B	88	6	51	49	54	46
4	200 mg Powder	C	85	20	62	38	14	86
5	400 mg Pellets	C	90	30	76	24	37	63

115 °C and at only 1 atmosphere. To obtain the same selectivity in a conventional batch or fixed-bed reactor system would require a higher reaction temperature (above 150 °C) [13,14]. It is not clear the effect that a high benzene:propylene molar ratio, such as the one used in the reactive separation, (22:1) would have in a conventional batch or fixed bed system. The stability of the catalyst with reaction time remains to be studied, as the main drawback of the use of highly active zeolites in cumene production is their quick deactivation [13].

Our system also reduces the additional time and energy needed to separate the benzene from the cumene mixture. In a conventional system for production of cumene where the reaction occurs with no simultaneous separation, such as in a batch reactor or a fixed-bed, all the cumene produced becomes intermixed with the byproducts and with the unreacted benzene, and the benzene needs to be separated from the cumene mixture. Although additional studies are required to optimize the performance of the catalytic separation process, the catalytic reaction and separation is attractive because of the energy-savings created by its high selectivity (85% and above) at relatively low temperatures (115 °C) and atmospheric pressure, and because it partially separates the reactants from the products as they form.

4. Conclusion

A novel reactor design has been completed and tested for catalytic separation production of cumene. This glass/stainless steel combination reaction system uses the inherent differences in boiling points between reactants and products to do one-step catalytic reaction and primary separation (for purification) at one atmosphere. We have demonstrated its design in the production of cumene from propylene and benzene. In these tests we studied catalyst morphology and reactant injection port locations. Testing of different reactor configurations for cumene production using both powdered and pelletized zeolite Beta catalysts helped in initial optimization of design and production yields. These initial studies showed that this design allowed for selectivity for catalytic separation reactions starting at 85% and above at the relatively low reaction temperature of 115 °C. Simultaneously, cumene reaction yield up to 30% was achieved with up to 76% of the unreacted benzene was separated from the products. Efficiency in this design and reaction route includes elimination of one cumene distillation process step, and recycling of benzene from reactant collection site (top of reactor) into the front-end process step. Continuing research is focused on both optimizing cumene yield through catalyst studies and reactor configuration, and applications of this design to other energy intensive hydrocarbon productions.

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