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Selective synthesis of cumene by isopropylation of benzene using catalytic membrane reactor

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ABSTRACT

Selective isopropylation of benzene to cumene is demonstrated using catalytic membrane reactor (CMR), to our knowledge for the first time and the performance was evaluated against conventional plug flow reactor (PFR). Almost complete elimination of byproducts like polyalkylated benzene and higher aromatics could be made possible by using CMR. These are present in significant amount when reaction is carried out with PFR. The cumene selectivity increased up to a maximum of 97.25% by CMR as against 90.05% with conventional PFR. The effect of reaction parameters that can greatly influence the process economics, such as liquid hourly space velocity (LHSV), reactant mole ratio and catalyst/reactor volume ratio were investigated. Changes in these parameters made for CMR are industrially advantageous. The process by CMR is more economical and ecofriendly than PFR as far as milder process parameters (higher LHSV, lower reactant feed mole ratio, less catalyst require, etc.) and process intensification (reaction and separation in single reactor) are concerned. The study provides new insights for benzene isopropylation reaction.

1. Introduction

Cumene is generally prepared by alkylation of benzene with isopropylene or isopropanol by Friedel–Craft alkylation route [1]. It is widely used as a precursor for the manufacture of phenol, acetone, α-methyl styrene, etc. Various processes are demonstrated in the literature for the preparation of cumene. Friedel–Craft alkylation reaction is catalyzed by either protonic acids (e.g., H_3PO_4) or lewis acids (e.g., BF_3) on various supports like amorphous or crystalline aluminosilicates. The reaction proceeds through dehydration of an alcohol to alkene then react via a carbonium ion mechanism with gas-phase benzene to produce cumene. Isopropylation of benzene can be a liquid-phase catalytic reaction [2].

Two processes most widely used on industrial scale are UOP's Cumox process [3] and Monsanto–Lummus Cumene process [4]. The Cumox process uses mixture of propylene and excess benzene reacted in the presence of solid phosphoric acid as a catalyst. The process offers 99.3% (by weight) conversion of propylene with 92.5% selectivity to cumene. In Monsanto–Lummus process, dry benzene and propylene are mixed in the alkylation reactor with $AlCl_3$–HCl catalyst. The main feature of this process is low benzene recycle ratio. A commercial process using zeolite catalyst is also demonstrated [5–8] that uses isopropanol, benzene and a heterogeneous catalyst—zeolite β.

Processes documented in the literature have several drawbacks like high catalyst volume, high reaction temperature, high feed mole ratio (high benzene in the feed than required), lower space velocity, lower yields, byproduct formation leading to higher capital and operational costs corrosion problems, etc.

In the present work, we have demonstrated a novel process for the preparation of cumene that uses the concept of catalytic membrane reactor (CMR). The main objective behind using CMR was to reduce the drawbacks in current processes. The reaction between benzene and isopropanol was investigated and the performance of CMR was evaluated vis-à-vis conventional plug flow reactor (PFR) using zeolite β as the catalyst. The most significant features of other processes that are being practiced on industrial scale (Monsanto and Cumox) are also compared with CMR.

Abbreviations: PFR, plug flow reactor; CMR, catalytic membrane reactor; IPA, isopropyl benzene; DIPB, diisopropyl benzene; HBF, high boiling fractions; LHSV, liquid hourly space velocity h^{-1}; GC, gas chromatography; FID, flame ionization detector; L, length of catalyst bed; D, diameter of reactor.

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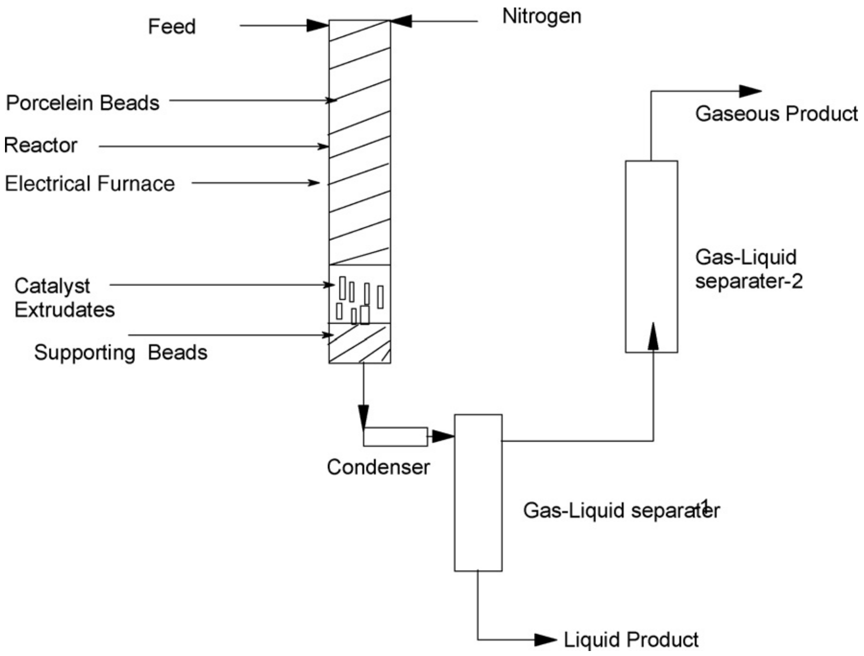

Fig. 1. Experimental conventional plug flow reactor (PFR) set up.

2. Experimental

2.1. Chemicals

Isopropanol, benzene, cumene and diisopropyl benzene (DIPB) (all >99% pure) were procured from s.d. Fine Chemicals Ltd., Mumbai and used without further purification.

2.2. Catalyst

Silica to alumina molar ratio of zeolite β is generally between 10 and 200. In this work, the large pore-12 embarked ring zeolite β having BET surface area of 250 m^2/g and Si/Al ratio in the range of 26–30 was used.

2.3. Process for cumene preparation by PFR and CMR

The experiments using PFR (Fig. 1) as well as CMR (Fig. 2) were carried out at similar temperature (210 °C) and time (5 h) in order to be able to better compare the performance of both methods. A SS316 fixed bed cocurrent down flow reactor is used in the present investigation. This reactor also has a special arrangement to equip the membrane, which is made of proprietary material. The zeolite β as a catalyst in powder form was coated on the membrane having 70-μm thickness and same catalyst layered membrane was rested on SS316 circular plate having 0.5-mm holes across the cross-sectional area. The same SS316 plate having membrane with coated catalyst powder was sealed with flanges at the bottom of the reactor. The small size porcelain beads were kept at the top portion of the reactor, which is the preheating zone of the reactor. The complete assembly is enveloped in electrical heating shell. Each shell is connected by the K-type thermocouple to measure catalytic membrane bed temperature. The outlet stream of the reactor was connected to the isothermal gas–liquid separator in order to separate the product cumene from benzene (Figs. 1 and 2).

In the beginning, catalyst was activated at 220 °C in presence of air for 5–6 h and then under running nitrogen for half an hour. The desired quantity of feed (isopropyl alcohol and benzene) was pumped to the reactor by using ISCO syringe pump. Care was taken to preheat reactants at 210 °C and get completely mixed prior to reaction on the catalyst surface. Samples were withdrawn from the reactor at defined time intervals and were analyzed using gas chromatography (Shimadzu model, FID detector with hydrogen as a carrier gas, using xylene master column). The sets of conditions used for carrying out cumene synthesis by PFR and CMR routes are given in Table 1.

3. Results and discussion

Initially, the reaction using PFR was carried out as per the reported procedure [5–8]. The reaction conditions were chosen based on maximum possible IPA conversion and cumene selectivity. The results obtained in the present work by PFR route were in agreement with the reported ones and are summarized in Table 2.

In PFR, the catalyst is always in some shape (extrudate, tablet) and size with some binder, which creates the diffusional resistance and increase catalyst loading. In present work, catalyst used is in extrudate form of 2 mm × 3 mm irregular size with alumina as a binder having catalyst:binder ratio of 80:20.

Table 1
Reaction conditions for PFR and CMR

Parameter	Conventional PFR	Vertical CMR (I)	Vertical CMR (II)	Vertical CMR (III)
Mole ratio (IPA:benzene)	1:6.5	1:2	1:3	1:3
Catalyst/100 cm^3 (reactor volume)	4.4	3.0	2.6	2.2
LHSV (h^{-1})	2.5	3.6	3.6	2.4
Reaction temperature (°C)	210	210	210	210

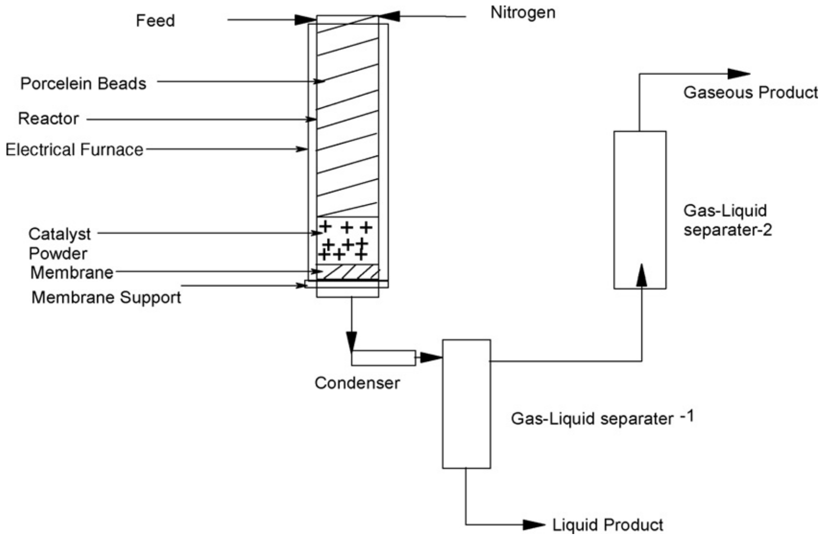

Fig. 2. Experimental proposed catalytic membrane reactor (CMR) set up.

In case of CMR, the catalyst is in powder form without any binder and layered on the membrane, which reduces diffusional resistance, increases the rate of mass transfer with reaction and reduces the catalyst loading. This advantages of CMR, makes the process parameters milder. The higher space velocity, lower molar ratio of isopropanol to benzene gives equivalent or enhances activity/selectivity as compared to PFR.

The experiments with CMR were carried out at similar temperature and time as for PFR. Other parameters viz; space velocity, feed mole ratio and catalyst volume were systematically varied in order to analyze their effect in case of CMR vis-à-vis PFR. The two parameters: temperature and time were kept same for both PFR and CMR so that the effect of other parameters can be better analyzed for a given catalyst. Variation of parameters was done also by considering their significance on process economics.

The progress of the reaction was monitored periodically by collecting samples after 1-h interval. It was noted that the reaction was stabilized after 3-h duration (as judged by the consistency in product distribution by GC analysis). These stabilized results are reported here as given in Table 2.

3.1. Reaction with PFR

The experiment was carried out at process parameters: 210 °C, LHSV of 2.5 h^{-1}, feed mole ratio (benzene:IPA) of 1:6.5, and catalyst: reactor volume of 4.4. The reaction was performed for a time on stream of 5 h. GC analysis of the product stream is given in Table 2. As seen from this table, byproducts formed were aliphatics, toluene, C_8 aromatics, *n*-propyl benzene and high boiling fractions (HBF). Similar type of product distribution is reported in the literature [5–8]. Table 3, gives the percent conversion based on each reactant. IPA and benzene conversion were found to be 99.8% and 11.87%, respectively. The cumene selectivity was observed to be 90.05%. Formation of other byproducts accounts to isopropanol conversion of 99.8%.

This reaction by PFR needs high amount of benzene to be taken in the feed. It was reported that at lower feed mole ratio, formation of DIPB increases [6]. The benzene dilution also helps to prolong the life of the catalyst. An excess of benzene coming out along with the product stream gets separated in the flash system, which is recycled back to the alkylation reactor. Cumene as a major product is separated in the fractionation column. The bottom from the fractionator is high aromatic materials containing mainly DIPB isomers. This DIPB needs to be reacted back with benzene in order to obtain cumene in a transalkylation reactor.

3.2. Reaction with CMR

In the case of CMR, three sets of conditions (I, II and III) were studied as given in Table 1. The parameters varied were space velocity (LHSV), feed mole ratio and catalyst:reactor volume ratio. The space velocity is based on the catalyst loaded (g) in powder form as a layer on the membrane. The product profile by GC and the percent conversions by CMR are given in Tables 2 and 3, respectively.

In all cases, the reaction was carried out at 210 °C and for 5 h as like in PFR. In idealized case of membrane reactor for cumene synthesis, the formed product should leave the reactor volume as and when it is formed. The membrane used in the present work is polymeric membrane of 70-μm size. The catalyst is in powder form and coated as a layer on the membrane. Once cumene is formed by catalytic reaction, due to less catalytic bed, cumene comes out of catalyst bed immediately and minimize the fur-

Table 2
GC product distribution in PFR and CMR

GC product distribution (wt.%)	Conventional PFR	Vertical CMR (I)	Vertical CMR (II)	Vertical CMR (III)
Aliphatics	0.17	2.26	0.84	0.65
Benzene	82.40	69.01	75.64	76.37
Cumene	15.85	28.64	23.47	22.98
Tol. + C_8 aromatics	0.30	0	0	0
n-Propyl benzene	0.07	0	0	0
C_{10-11} aromatics	0.09	0	0	0
DIPB	1.01	0	0	0
HBF	0.11	0	0	0

Table 3
Performance comparison of PFR and CMR

Performance	Conventional PFR	Vertical CMR (I)	Vertical CMR (II)	Vertical CMR (III)
IPA conversion (wt.%)	99.8	97.74	99.16	99.35
Benzene conversion (wt.%)	11.87	18.93	15.27	14.46
Cumene selectivity (%)	90.05	92.68	96.54	97.25

Benzene in feed: 93.49% (PFR, 1:6.5); 85.12% (CMR-I, 1:2); 89.27% (CMR-II and -III, 1:3). % IPA conversion: (100 − aliphatics in product). % Benzene conversion: [(Benzene in feed) − (Benzene in product)/(Benzene in feed)] × 100.

ther reaction of cumene alkylation to DIPB and HBF. The presence of membrane removes selectively only cumene and not DIPB or HBF. This continuous removal of formed products would shift the reaction equilibrium in the forward direction (Le Chateliers principle). This implies a possibility of increasing feed rate (LHSV) than for PFR. Continuous removal of formed products in CMR eliminates possibility of (i) cumene reacting further with isopropanol leading to multialkylation and (ii) the catalyst poisoning. Furthermore, by operating in a reaction pressure-driven permeation (at higher LHSV) mode, external and pore diffusion effects may be practically eliminated and a desired catalyst contact time is made possible. This might be useful in maximizing selectivity. Because of the reduced catalyst contact time, an amount of catalyst required can also be reduced. The reduced catalyst volume may also lead to reduction in byproduct (DIPB) formation. In CMR, the integration of heat exchange with catalytic reaction is possible, that is not readily realized with PFR. The heat evolved from the catalytic reaction might be useful for the separation of the reaction products.

3.3. *Variations in reaction parameters in CMR*

Three sets of conditions are studied as given in Table 1. In case of set I, the feed ratio was decreased to 1:2, the catalyst volume decreased to 3.0 and LHSV was elevated to 3.6 h^{-1}. In this case, DIPB or higher aromatics formation was found to be nil, but considerable amount of aliphatics were observed. The possible reason could be that (i) at lower feed ratio of 1:2, the benzene quantity may not be adequate, which may lead to conversion of IPA to lower boiling fraction and (ii) the reaction time may not be sufficient. These postulations need further experimental validation, which is in progress. The cumene selectivity in this case reached to 92.68%. In case of II, the feed ratio was increased to 1:3 and catalyst volume decreased to 2.6, keeping LHSV same as in I. It was thought to observe the effect of simultaneous lowering of catalyst volume and increase in benzene content in feed on the aliphatics formation. Reaction conditions in set II resulted in lowering of aliphatic formation, but could not eliminate completely. Thus lowering of catalyst and increase in benzene content as in set II may not be enough to completely eliminate the aliphatic formation. In other words, there may be additional factors responsible for formation of aliphatics. There was no DIPB or higher aromatics formation. In order to explore the possibility of further lowering down the aliphatic formation, reaction conditions in the set III were further modified. The feed ratio was kept same as in II, but catalyst volume was lowered to 2.2 and LHSV to 2.4 h^{-1}. These variations led to small reduction in the aliphatic formation (Table 2). This indicates the necessity of further modifications in the reaction condition.

In all the three sets of CMR, there was no formation of DIPB or high boiling fractions. The possible explanation could be that the formed cumene gets desorbed from the catalyst surface and carried away by the membrane (since it has higher sorption capacity for cumene). This possibly avoids further sequential reaction of cumene with IPA to give DIPB or high boiling fractions.

3.4. *Effect of space velocity*

In CMR, the effect of space velocity was studied by initially increasing it up to 3.6 h^{-1} in sets I and II as against 2.5 h^{-1} in the PFR. This increased space velocity may help to increase the cumene selectivity to 92.68% and 96.54%, as against 90.05% in PFR at almost identical IPA conversion. Higher LHSV may be helping in elimination of sequential reaction of cumene isopropylation to DIPB or high boiling fractions [6]. The increase in space velocity would also increase the life of the catalyst by reducing reactant–catalyst surface contact time (residence time). The decreased residence time ultimately increases per pass conversion. In case of III, the space velocity was lowered (to 2.4 h^{-1}) than in first two sets of CMR, but was almost identical as that of PFR. This LHSV of 2.5 h^{-1} for PFR was reported to be the best for obtaining maximum cumene selectivity [6]. This lowering of LHSV in set III was done in order to examine the change in aliphatic formation. It can be hypothesized that in case of higher LHSV (first two cases), the reactant may not get sufficient time for the reaction, and thus lead to aliphatic formation. The membrane being selective towards hydrocarbons, the formed aliphatic also gets permeated through the membrane. If LHSV is lowered, the reactant may be exposed to catalyst for sufficient time possibly leading to reduction in aliphatic formation. The qualitative trend was observed in lowering the aliphatic formation by reducing LHSV in III case. This needs further investigations. The cumene selectivity was increased up to 97.25% in set III as against 90.05% in PFR, at the identical IPA conversion. The higher LHSV, helps in prolonging the life of the catalyst. This eventually leads to reduction in catalyst replacement and/or catalyst regeneration cycle lost and also in byproduct separation cost. This has high impact on process economics by minimizing the cycle of plant shut down and saving in other plant utilities. The reduction in byproduct formation reduced the separation cost.

3.5. *Effect of reactant mole ratio*

The reactant (IPA:benzene) mole ratio was taken as 1:2 in set I and 1:3 in sets II and III as compared to 1:6.5 with conventional PFR, as given in Table 1. As the IPA concentration over the catalyst surface increased, the relative formation of *n*-propyl and DIPB increased proportionately [6]. In CMR, the continuous removal of products eliminates its possibility of reacting further with isopropanol leading to multialkylation of cumene to form DIPB. Ultimately, this avoids excess benzene recovery and reduces the benzene recycle cost.

3.6. *Effect of catalyst/reactor volume ratio*

An amount of catalyst used for experiments by CMR is nearly half than for PFR. By operating in a reaction pressure-driven permeation (at higher LHSV) mode, external and pore diffusion effects may be practically eliminated and desired catalyst contact times are made possible. This might be useful in maximizing selectivity with minimal contact time and thus catalyst volume. This reduction in

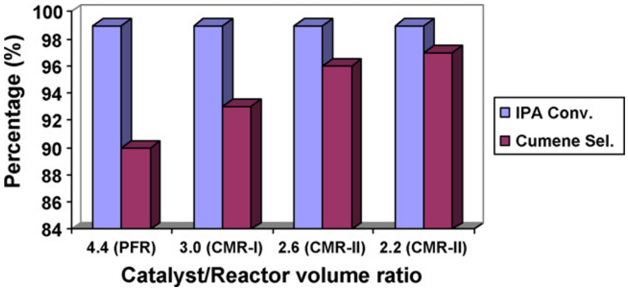

Fig. 3. Comparison of PFR and CMR.

catalyst volume gives, a high impact on the process economic with respect to saving in catalyst quantity, reactor volume cost, etc.

As seen in Fig. 3, the IPA conversion for PFR and CMR though is same; the cumene selectivity is increased gradually from PFR to all three sets of CMR. This figure indicates that the reaction conditions for CMR III are better than others. Though, set III may not be optimum and needs further experimentation in order to further eradicate certain drawbacks like aliphatic formation, possible reduction of benzene: IPA ratio to its ideal value of 1:1, increase in LHSV, etc.

4. Comparison with presently used processes

Current processes being practiced for cumene production (mainly UOP's Cumox process [3] and Monsanto–Lummus Cumene process [4]) use excess benzene in the feed, which is separated by flash condensation and then recycled. Formed cumene needs to be separated using distillation columns. Isomers of DIPB are formed as byproducts, which are separated and then transalkylated to cumene. Isomers of DIPB are formed as byproducts, which are separated and then transalkylated to cumene. This involves additional transalkylation reactor set up. The catalyst used in some of the processes is a strong acid. It is corrosive and creates environmental pollution. In such process, reactor effluent needs to be washed with water and caustic in order to separate organics. In addition, water needs to be added to keep the catalyst away from becoming friable and disintegrating. The process using zeolite catalyst suffers from certain drawback like requirement of higher catalyst volume, higher reactant mole ratio and byproduct formation (DIPB isomers, toluene, C_{8-11} aromatics, *n*-propyl benzene and high boiling fractions).

The significance of catalytic membrane reactor is that the reduction in feed mole ratio, increase in LHSV, reduction in catalyst volume and complete elimination of higher aromatics could be achieved. This invention thus makes the benzene isopropylation to cumene process better economical and eco-friendly.

5. Conclusion

The significant outcomes of this most interesting research using CMR, can be summarized as:

(1) Total elimination of higher aromatic byproducts made achievable.
(2) The 50% reduction in catalyst requirement as compared to conventional PFR.
(3) The feed dilution is significantly reduced. This leads to saving of benzene and reduction in recycle equipment and operating cost.
(4) LHSV could be elevated to 3.6 h^{-1} as against 2.5 h^{-1} with conventional PFR.
(5) The amelioration of catalyst poisoning is achieved.
(6) The integration of separation and purification steps with catalytic reaction could be used.
(7) In CMR, the integration of heat exchange with catalytic reaction is benefited, that is not readily realized with PFR.
(8) In view of the industrial scale up, capital cost for separation equipments and its accessories are considerably reduced, which are otherwise essential in case of PFR.
(9) The present study provides new insights for benzene isopropylation to cumene process.

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