Alkylation of phenol with MTBE and other tert-butyl ethers: cation exchange resins as catalysts

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Alkylation of phenol was carried out using methyl tert-butyl ether, mono tert-butyl ether of mono ethylene glycol, tert-butanol and isobutylene in the presence of cation exchange resins, acid treated clay and para-toluene sulfonic acid as catalysts. The selectivity with respect to 2- and 4-tert-butyl phenol was studied.

Keywords: Cation exchange resin; phenol; methyl tert-butyl ether (MTBE); alkylation; tert-butyl phenols

1. Introduction

tert-butyl phenols are widely used as antioxidants. They are usually produced by reacting pure isobutylene or C_4 fraction from naphtha crackers, which contains isobutylene, with phenol over acid catalysts. With an increase in the production of methyl tert-butyl ether (MTBE) for use as an antiknock and octane number booster for gasoline, MTBE appears to be an attractive source, for in situ generation of pure isobutylene, for alkylation of phenol. It also avoids the problems associated with the transportation and storage of the C_4's.

The decomposition of MTBE for the production of pure isobutylene gas has been a subject of detailed studies [1–3]. This work was undertaken to study the alkylation of phenol directly with MTBE in the presence of cation exchange resins as catalysts.

2. Literature survey

A survey of the literature shows that no detailed studies have been made on the

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alkylation of phenol with MTBE. Most of the work reported is in the form of patents. Macho et al. [4] have studied the possibility of using, among other reagents, alkyl tert-butyl ethers for the alkylation of phenol. They studied the reaction using Ostion KS cation exchange resin and a phosphate catalyst. Crozat et al. [5] have claimed to have obtained tert-butyl phenols from reaction between phenol and MTBE (1 : 1 mol ratio) in the presence of ~ 10% Amberlyst 15 as catalyst. They have reported a ratio of 2- : 4-tert-butyl phenol (2- : 4-TBP) of ~ 0.5 at 63.8% conversion of phenol. Schulz et al. [6] have claimed a yield of 95% 4-TBP on reacting 1 mol each of phenol and MTBE in the presence of 1 mol H_2SO_4 as catalyst. A highly selective method to obtain 4-TBP has been reported by Sartori et al. [7] using $ZrCl_4$ as catalyst. They used 0.1 mol of catalyst for 0.1 mol each of phenol and MTBE.

The use of MTBE for the alkylation of substituted phenols has also been reported [8–11]. Merger et al. [8] and Ancillotti et al. [9] have also used other alkyl tert-butyl ethers for the alkylation of phenol. There is apparently no literature on the use of mono- or di-tert-butyl ethers of mono ethylene glycol or propylene glycol for the alkylation of phenols.

3. Experimental

The macroporous cation exchanger resin, Amberlyst 15 was obtained from Rohm and Haas Co., USA, and the macroporous monodisperse K-2661 from Bayer, Germany. Nafion NR50 was obtained from Du Pont, USA, and the macroporous Indion 130 from Ion Exchange (India) Ltd., India. The acid treated clay catalyst, Engelhard F-24, was obtained from Engelhard, USA. The resin catalysts were washed with acetone and dried at 100°C under vacuum (1–2 mm Hg) for 4–5 h before use. *p*-toluene sulfonic acid (PTSA) and phenol were obtained from S.d. Fine Chem. Pvt. Ltd., India. MTBE was obtained from Fluka, Germany. tert-butanol was obtained from HÜLS, Germany. Isobutylene gas cylinder was obtained from British Oxygen Limited, UK. Mono tert-butyl ether of mono ethylene glycol (MEGMTBE) was prepared in the laboratory by acid catalyzed etherification of MEG with tert-butanol. The purity of all the chemicals was $\geqslant 99\%$. The physical properties of the cation exchange resins and acid treated clay catalysts are listed in table 1.

All the experiments were carried out in a 1×10^{-4} m^3 stainless steel autoclave (i.d. = 0.03 m) manufactured by Parr Instruments Company, USA. A pitched four-bladed turbine impeller was used for agitation. The temperature was maintained at ±0.5 K of the desired value with a built in PID temperature controller.

Analysis of the samples was done using a gas chromatograph (Chemito 8510, Toshniwal Brothers Pvt. Ltd., India) with a flame ionization detector. A 4 m stainless steel column packed with 10% OV-17 supported on Chromosorb WHP was used. The injector and detector were kept at 673 K. The oven temperature was pro-

Table 1
Properties of different catalysts

Physical property	Amberlyst 15	Nafion H NR-50	Monodisperse K2661	Engelhard F-24	Indion 130
shape	beads	beads	beads	granular	beads
size (mm) (min 90%)	0.5	1.5	0.6	0.66	0.55
internal surface area (m^2/g)	55.0	~ 0.003	40.0	350.0	a
weight capacity (meq/g)	4.75	0.8	1.35	0.3	5.0
cross-linking density (% DVB)	20–25	b	14–25	b	a
porosity (vol%)	36.0	non-porous	50.0	32.0	40.0
temperature stability (°C)	120	200	130	a	150

[a] Data not available.
[b] Not applicable.

grammed as follows: 150 s at 373 K, 0.5 K/s ramp rate up to 353 K, 90 s at 353 K, 0.17 K/s ramp rate up to 513 K and 600 s at 240 K. Nitrogen gas was used as the carrier gas and the flow rate was maintained at 0.5×10^{-6} m^3/s. The samples withdrawn were analyzed for phenol and tert-butyl phenols only because a part of MTBE and isobutylene gas could be in the vapour phase and the analysis of these based on the liquid samples would not be representative.

4. Results and discussion

MTBE cracks in the presence of the acid catalyst producing isobutylene and methanol [12]. Isobutylene thus produced reacts in situ with phenol giving tert-butyl phenols (TBPs) and phenyl tert-butyl ether (PTBE). A very small amount of diisobutylene (DIB) was formed which further cracked and reacted with phenol as the reaction proceeded. The formation of DIB is an unsteady process which goes through a maximum and decreases with time [13].

Alkylation of phenol may be considered an irreversible and concurrent reaction at low temperatures [14]. The reaction network is shown in fig. 1. Phenol acquires a negative charge and is preferentially adsorbed in the catalyst pores as compared to MTBE, which is non-polar [15]. The amounts of 2,6-DTBP and 2,4,6-TTBP formed are very low as compared to 2,4-DTBP. Due to the bulkiness of 2-TBP and 2,4-DTBP molecules, the formation of 2,6-DTBP and 2,4,6-TTBP becomes difficult in the pores. PTBE can crack in the presence of acid catalysts even at low temperatures and hence the final product mixture does not contain any PTBE [16].

There was no change in the overall rate of reaction of phenol when the speed of agitation was varied from 1000 to 1500 rpm. Thus in this range, the resistance due to external mass transfer was eliminated.

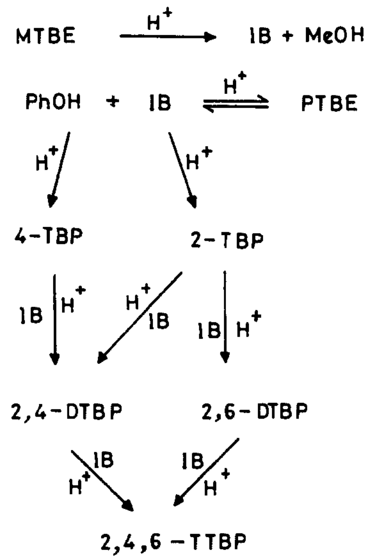

Fig. 1. Reaction scheme for alkylation of phenol with MTBE. MTBE: methyl tert-butyl ether; IB: isobutylene; MeOH: methanol; PhOH: phenol; TBP: tert-butyl phenol; DTBP: de tert-butyl phenol; TTBP: tri tert-butyl phenol.

The effect of temperature on the overall rate of conversion of phenol was studied in the range of 30 to 56°C. It was observed that the 2- : 4-TBP ratio in the products increased from 1.29 to 1.45 as the temperature was raised from 30 to 56°C. It appears that the formation of 2-TBP has higher activation energy. A similar effect was observed by Unni and Bhatia [17] for alkylation of phenol using isobutylene in the presence of Amberlyst 15 as catalyst. The activation energy for the formation of 2,4-DTBP is lower than that for 2- and 4-TBP [17]. With a rise in temperature, the rates of formation of 2- and 4-TBP were found to increase. This increase in the formation of 2- and 4-TBP may favour the formation of 2,4-DTBP via the consecutive reaction. The product distributions are given in table 2.

The catalyst loading was varied from 5 to 20% w/w of the reactants. Upto ~ 10% loading, the overall rate of reaction of phenol increased with an increase in the catalyst loading. Beyond 10%, there was a levelling off of the overall reaction rate.

The effect of various catalysts on the conversion and product distribution is given in table 3. When monodisperse K2661 was used as the catalyst, the overall rate of reaction of phenol was higher than that obtained with Amberlyst 15 as catalyst. The ratio of 2-TBP : 4-TBP was 1.45 for both the catalysts. The rate of reaction using Nafion NR50 was very low. For the same catalyst loading, the number of H^+ ions is lower for Nafion NR50 than for Amberlyst 15 and, moreover, the internal surface of the Nafion NR50 beads is very much lower than that of Amberlyst 15 (table 1). The higher selectivity for *o*-isomer with Nafion may be due to the special structure of this resin, which can adsorb phenol and provide a "porous"

Table 2
Effect of temperature on product distribution and conversion of phenol [a]

Temp. (°C)	Reaction time (h)	Conversion of phenol (%)	Product distribution						*o*-/*p*-TBP
			PTBE	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	
30	12	26.8	0.72	48.52	37.76	1.38	11.41	0.21	1.29
45	8	31.8	0.27	48.56	36.49	0. 84	13.52	0.33	1.33
56	6	31.1	0.00	48.08	33.11	1. 47	17.34	0.00	1.45

[a] Phenol : MTBE = 2 : 1, 20% (w/w) loading Amberlyst 15, 1000 rpm, autoclave 100 ml.

Table 3
Effect of catalyst on conversion of phenol and product distribution [a]

Catalyst	Reaction time (h)	Conversion of phenol (%)	Product distribution						*o*-/*p*-TBP
			PTBE	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	
A-15	6	31.1	0.00	48.08	33.11	1.47	17.34	0.00	1.45
F-24	6	22.2	0.00	37.19	52.39	0.24	9.86	0.32	0.71
K-2661	2	31.4	0.74	51.26	35.38	1.07	11.56	0.00	1.45
*p*TSA	3	30.7	0.43	43.88	40.58	1.97	12.44	0.70	1.08
NR-50	11	29.7	0.00	47.19	20.59	3.16	25.42	3.63	2.29

[a] Phenol : MTBE = 2 : 1, temp. 56°C, 20% (w/w) loading catalyst, PTSA eq. to 20% (w/w) loading A-15, 1000 rpm, autoclave 100 ml, A-15: Amberlyst 15; NR-50 Nafion NR-50; F-24: Engelhard F-24; *p*TSA: *p*-toluene sulfonic acid; K2661: monodisperse K2661.

structure [18]. As compared to Amberlyst 15, the homogeneous catalyst *p*-TSA gave a lower 2- : 4-TBP ratio of 1.08. The acid treated clay Engelhard F-24 gave a 2- : 4-TBP ratio of only 0.71 and the overall rate of reaction of phenol using this catalyst was significantly lower as compared to the rate obtained when Amberlyst 15 was used as the catalyst.

The Amberlyst 15 catalyst particles were milled to ~ 0.1 mm to study the effect of pore diffusion. It was observed that the percentage conversions of phenol in 6 h using ~ 0.5 and ~ 0.1 mm particles were ~ 31 and ~ 38% respectively. This seems to indicate the presence of macroporous diffusion resistance. The ratio of 2- : 4-TBP was higher when coarser particles were used as catalysts. The effect of particle size was also studied using Indion 130 of two sizes, ~ 1.0 and ~ 0.3 mm, at 8% (w/w) loading. The overall conversion of phenol in 6 h using coarse and fine catalyst particles was ~ 25 and ~ 30% respectively. The product distributions are given in table 4.

The mole ratio of phenol : MTBE was varied from 1 : 2 to 3 : 1. It was observed that as the phenol : MTBE mole ratio was increased, the 2- : 4-TBP ratio increased. However, contrary to expectations, with lower phenol : MTBE mole ratio, a lower amount of 2,4-DTBP was formed. The product distribution obtained using different mole ratios of phenol : MTBE is given in table 5.

Various alkylating agents were used for tert-butylation of phenol. The product distributions at ~ 30% conversion of phenol using MTBE, MEGMTBE, *t*-butanol and isobutylene were similar. However, the overall rate of reaction of phenol varied with the alkylating agent. The overall rate of reaction with different alkylating agents was found to decrease in the following order: isobutylene > MEGMTBE > MTBE > tert-butanol. It is clear from the above observations that the mechanism for tert-butylation of phenol is the same for all alkylating agents. Table 6 shows the product distributions obtained for different alkylating agents used. It appears that the in situ generation of methanol and mono ethylene glycol in the case of MTBE and MEGMTBE does not influence the product distribution as compared to alkylation with isobutylene under otherwise comparable conditions.

It is known that the presence of water in the reaction mixture can have a detrimental effect on the reaction. Hence experiments were performed with 1 and 2% water content in the reaction mixture. It was observed that with 1% water content, there was no significant change in the overall rate of reaction of phenol. At higher water content (2%) the percent conversion of phenol in 6 h dropped from ~ 31 to ~ 25%. The product distributions, however, were similar.

Solvents are generally believed to greatly influence the rate and selectivity of a reaction. Hence, an experiment was carried out with 50% w/w toluene. The catalyst loading was maintained at 20% w/w of phenol and MTBE. There was no effect of solvent on either the rate of reaction or the product distribution. Phenol being polar may be preferentially adsorbed on the catalyst and hence toluene may not have any significant effect.

Table 4

Effect of catalyst on conversion of phenol and product distribution[a]

Catalyst	Catalyst[b] size (mm)	Reaction time (h)	Conversion of phenol (%)	Product distribution						*o*-/*p*-TBP
				PTBE	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	
A-15	~ 0.5	6	31.1	0.00	48.08	33.11	1.47	17.34	0.00	1.45
A-15	~ 0.1	1	29.0	0.39	46.91	43.70	1.18	9.101	0.00	1.10
I-130	~ 1.0	8	26.7	0.00	53.55	34.16	1.25	9.54	0.50	1.57
I-130	~ 0.3	4	29.9	0.00	50.71	40.57	1.28	7.26	0.17	1.25

[a] Phenol : MTBE = 2 : 1, temp. 56°C, 1000 rpm, autoclave 100 ml, A-15: Amberlyst 15 (20% w/w loading), I-130: Indion 130 (8% w/w loading).

[b] Average catalyst size.

Table 5

Effect of mole ratio of phenol : MTBE on product distribution[a]

Mole ratio (phenol : MTBE)	Reaction time (h)	Conversion of phenol (%)	Product distribution						*o*-/*p*-TBP
			PTBE	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	
2 : 1	6	31.1	0.00	48.08	33.11	1.47	17.34	0.00	1.45
3 : 1	6	25.9	0.00	51.77	34.32	1.34	12.38	0.20	1.51
1 : 1	2	26.1	0.39	48.50	40.82	0.81	9.48	0.00	1.19
1 : 2	2.5	30.9	0.00	51.56	41.95	0.62	5.86	0.00	1.21

[a] 56°C, 20% (w/w) loading A-15, 1000 rpm, autoclave 100 ml, A-15: Amberlyst-15.

Table 6
Effect of alkylating agent on product distribution and conversion of phenol [a]

Alkylating agent	Reaction time (h)	Conversion of phenol (%)	Product distribution						*o*-/*p*-TBP
			PTBE	2-TBP	4-TBP	2,6-DTBP	2,4-DTBP	2,4,6-TTBP	
MTBE	6	31.1	0.00	48.08	33.11	1.47	17.34	0.00	1.45
MEGMTBE	3	28.8	2.10	47.55	32.45	1.59	15.20	1.11	1.47
t-butanol	10	30.3	1.65	53.30	32.06	1.53	11.46	0.00	1.44
i-butylene	35 min	27.1	0.00	46.77	31.89	1.58	18.48	1.28	1.47

[a] Phenol : alkylating agent = 2 : 1, 56°C, 20% (w/w) loading of A-15, 1000 rpm, autoclave 100 ml.

5. Conclusions

MTBE has been found to be a very effective tert-butylating agent. The selectivity and product distribution obtained using MTBE, MEGMTBE and tert-butanol for tert-butylation in the presence of Amberlyst 15 catalyst were found to be comparable with those obtained using pure isobutylene gas although the rates of reaction were lower. The selectivity with respect to 2-TBP was the highest in the presence of Nafion NR50 catalyst and lowest in the presence of Engelhard F-24 catalyst.

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