PREPARATION OF BUTYLATED PARA CRESOLS USING AMBERLYST-15

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Abstract: 2,6-di-*tert*-butyl-*p*-cresol or BHT is effective antioxidant and widely used in food industrial. BHT was prepared in a batch reactor via butylation of *p*-cresol and *tert*-butanol which used Amberlyst-15 as a catalyst. The reaction parameters were investigated as reaction temperature (80 °C -130 °C), *p*-cresol: *tert*-butanol mole ratio (1:2 - 1:20), catalytic amount (0 wt.% - 20 wt.% based on *p*-cresol weight) and reaction time (2 hrs.-10 hrs.). The quantitative analysis was examined by high-performance liquid chromatography (HPLC).

Introduction: The butylation of *p*-cresol is possible to form *C*- and *O*-alkylated products that depend on reaction condition such as reaction temperature and catalytic type. The strong acidic catalyst or high reaction temperature induces to *C*- alkylated products formation, while weak acidic catalyst or low reaction temperature lead to *O*-alkylated product formation.[1] Also, reaction optimization is important for the desired product selectivity. The formation of *C*-butylated *p*-cresol is consecutive with 2-*tert*-butyl-*p*-cresol formation and then followed by 2,6-di-*tert*-butyl-*p*-cresol which is generally called BHT (butylated hydroxytoluene).[2] BHT is a well known antioxidant in food industry as well as in jet fuels, petroleum products, cosmetics, pharmaceuticals, rubber, polymerization inhibitor, UV absorber and basic raw material for the manufacture of oil-soluble phenol-formaldehyde resins.[3-4]

Alkylation reaction can occur by Lewis and Bronsted acids catalysis that included homogenous and heterogeneous catalysts. In the case of homogeneous catalyst which causes equipment corrosion, handling and waste disposal problem. Therefore, heterogeneous catalyst is chosen to replace it. Amberlyst-15 is a sulfonic acid polymeric resin and one of the commercial heterogeneous catalysts. The advantages of Amberlyst-15 are high acidity, ease separation, less toxicity and non-corrosion.[5-6]

The present work studied the butylation of *p*-cresol over Amberlyst-15 catalyst with *tert*-butanol which is a by-product from propylene oxide production in the Atlantic Richfield Co. (ARCO) patent.[2] The study included effect of reaction temperature, mole ratio of *p*-cresol to *tert*-butanol, catalytic amount and reaction time on product yield and selectivity.

Methodology: Materials: *p*-Cresol (Sigma-Aldrich, 99%), *tert*-butanol (Fluka, >99%), 2-*tert*-butyl-*p*-cresol (Aldrich, 99%) and 2,6-di-*tert*-butyl-*p*-cresol (Merck, >99%) were used for alkylation reaction. Amberlyst-15 was purchased from Aldrich.

Reaction procedure: The alkylation of *p*-cresol with *tert*-butanol was carried out in the autoclave reactor, received from Parr instrument company. The reaction conditions were the *p*-cresol to *tert*-butanol mole ratio (1:2 - 1:20), the amount of catalyst (0 wt.% - 20 wt.% of *p*-cresol weight), the reaction temperature (80 °C - 130 °C) and the reaction time (2 hrs. - 10 hrs.) with the agitation speed at 200 rpm. The reaction mixture was collected and analyzed by 600Waters analytical high-performance liquid chromatography equipped with ultra C18 capillary column. The optimum conditions were considered based on the highest yield of di-butylated *p*-cresol.

Results, Discussion and Conclusion: The impact of the reaction temperature on the product yields and selectivity achieved from the butylation of *p*-cresol with *tert*-butanol as shown in

Table 1. The *p*-cresol was converted to mono- and di-butylated products increasing with raised reaction temperature from 80 ^oC to 120 ^oC. However, at further reaction temperature preferred the dealkylation of butylated products. Also, yield of di-butylated product was declined that might be transformed back to mono-butylated product at 130 ^oC. Moreover, the olefins that produced by dehydration of *tert*-butanol were possibly consumed in other parallel reactions such as alkylation, oligomerization and cracking. It was well known that oligomerization and cracking were foremost at high reaction temperatures.[7] The highest yield (46.0%) and selectivity of di-butylated product were obtained at reaction temperature 120 ^oC. This result showed 120 ^oC was an optimum reaction temperature.

Table 1. Effect of reaction temperature on product yields and product distribution over Amberlyst-15

Temperature (^oC)	%conversion	Alkylation yield (%)		Selectivity (%)
		Mono-	di-	mono : di
80	11.7	1.0	0.1	19.0 : 1
100	18.2	2.5	0.1	42.2 : 1
110	47.1	23.4	2.1	11.1 : 1
120	78.3	26.5	46.0	0.6 : 1
130	84.4	39.9	36.4	1.1 : 1

Reaction condition: *p*-cresol: *tert*-BuOH = 1:15 by mole, 10 wt% of Amberlyst-15 based on *p*-cresol, 8 hrs.

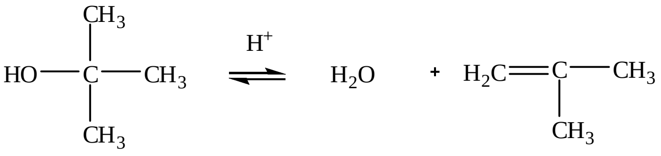
The reaction results in Table 2 indicated the influences of *p*-cresol to *tert*-butanol mole ratio on conversion and product distribution. The results revealed an increasing of the di-butylated product yield and selectivity when amount of butylating agent (*tert*-butanol) was enlarged from 1:2 to 1:20 by mole. On the other hand, mono-butylated product yield was decreased due to the transformation of mono- to di-butylated product.

Table 2. Effect of mole ratio on product yields and product distribution over Amberlyst-15

p-cresol : *tert*-BuOH mole ratio	%conversion	Alkylation yield (%)		Selectivity (%)
		Mono-	di-	mono : di
1 : 2	90.2	46.4	14.5	3.2 : 1
1 : 5	95.4	42.4	33.0	1.3 : 1
1 : 8	90.5	37.4	35.2	1.1 : 1
1 : 12	79.1	29.5	45.5	0.7 : 1
1 : 15	78.3	26.5	46.0	0.6 : 1
1 : 20	78.7	27.4	46.3	0.6 : 1

Reaction condition: 120 ^oC, 10 wt% of Amberlyst-15 based on *p*-cresol, 8 hrs.

In addition, a further increasing in mole ratio from 1:5 to 1:20 showed decreasing of conversion. This effect may be caused by the side reaction of excess *tert*-butanol as shown in Figure 1. Dehydration of *tert*-butanol led to isobutylene formation and subsequent oligomerization which produced diisobutylene and triisobuylene, respectively.



$$HO-C(CH_3)_2-CH_3 \xrightleftharpoons{H^+} H_2O + H_2C=C(CH_3)-CH_3$$

tert-Butanol Isobutylene

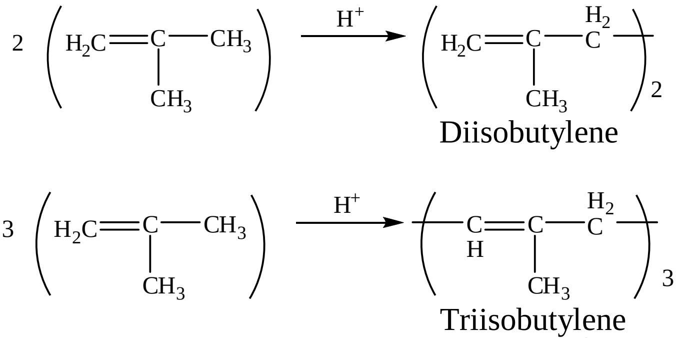


Figure 1. Side reaction of *tert*-butanol [2]

Subsequently, the effect of catalytic amount on conversion and product distribution was shown in Table 3. An increasing of catalytic amount from 0 wt.% to 10 wt.% could enhance the *p*-cresol conversion and product yields. The *p*-cresol barely transformed into butylated product under this reaction condition without catalyst. This result confirmed the acid catalyst was important to induce butylation reaction, as demonstrated in Figure 2. The greatest di-butylated product yield (46.0%) was obtained at the catalytic loading of 10 wt.% based on *p*-cresol. However, the conversion and di-butylated yield slightly decreased at the catalytic amount over 10 wt.% This might be caused by the catalyst overloading impeded the phase mixing of *p*-cresol, *tert*-butanol and catalyst. According to these results, catalytic amount at 10 wt.% was selected to be use in the next experiment.

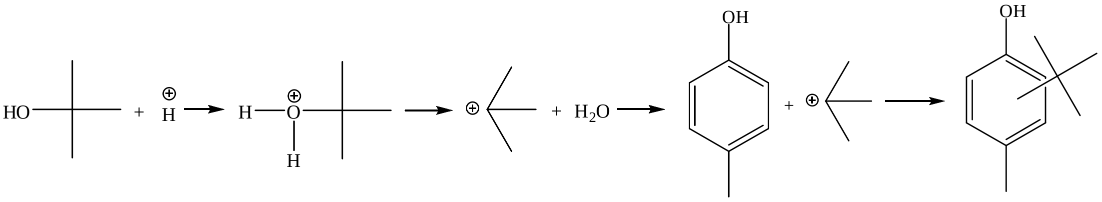


Figure 2. Acid catalysis of butylation reaction

Table 3. Effect of catalytic amount on product yields and product distribution over Amberlyst-15

Catalytic amount (wt.%)	%Conversion	Alkylation yield (%)		Selectivity (%)
		mono	Di	mono : di
0	4.0	0.1	0.00	-
5	74.3	31.0	42.6	0.7: 1
10	78.3	26.5	46.0	0.6: 1
15	73.6	29.8	36.3	0.8: 1
20	56.5	47.0	9.1	5.2: 1

Reaction condition: 120 ^{o}C, *p*-cresol: *tert*-BuOH = 1:15 by mole, 8 hrs.

The influence of reaction time on butylation was considered and showed in Table 4. The conversion and di-butylated product yield were enhanced with increasing of reaction time from 2 hrs. to 8 hrs. When the reaction was continued over 8 hrs., conversion and product yield were declined. Reaction result at 10 hrs. could be explained by dealkylation or elimination of butyl group that caused the product transformed back to *p*-cresol. Based upon these results, reaction time at 8 hrs. was selected to the optimum condition that contained 78% conversion with 46% di-butylated product yield.

Table 4. Effect of reaction time on product yields and product distribution over Amberlyst-15

Time (hrs.)	%conversion	Alkylation yield (%)		Selectivity (%)
		Mono	di	mono : di
2	57.22	37.23	0.94	39.61: 1
4	72.01	31.53	33.63	0.94: 1
6	75.57	30.98	45.53	0.68: 1
8	78.30	26.50	46.03	0.58: 1
10	77.58	20.37	33.31	0.61: 1

Reaction condition: 120 °C, *p*-cresol: *tert*-BuOH = 1:15 by mole, 10 wt% of Amberlyst-15 based on *p*-cresol

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