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# Separation of Individual Cresols from Mixed Cresols

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## Abstract

The emphasis of the present work was mainly to develop process conditions for a better yield and purity of *m*-cresol which is used as a starting material for the production of menthol. Experiments were conducted to isolate *m*-cresol by a sulfonation-desulfonation method. The various parameters studied included reaction temperature, weight ratio of cresols to sulfuric acid, and reaction time. The best conditions were reaction temperature 80°C, reaction time 5 h, and w/w ratio of cresols to sulfuric acid of 1:1. Under these conditions the conversion of *m*-cresol to *m*-cresol sulfonate was 96.5%. After desulfonation the overall recovery of the product *m*-cresol, based on the amount of *m*-cresol in the initial crude mixture, was 63%. The purity of the final product was more than 80%. The effects of various impurities (*o*-, *p*-cresols, and phenols) are discussed.

The problem of separation of cresol isomers has been studied since the 1920s. *o*-Cresol can be easily separated by fractional distillation from *m*- and *p*-cresols due to the appreciable difference in their boiling points. It is difficult, however, to separate *m*- and *p*-cresols from a cresol mixture due to their similar physical and chemical properties. The main use of methylated *p*-cresol is in the production of an antioxidant (2,6-ditertbutyl *p*-cresol), whereas *m*-cresol finds use as the starting material for the production of menthol.

In the past, attempts have been made to separate cresol mixtures. The various methods can be grouped under the headings extractive crystallization (*1–5*), adductive crystallization, clathration (*6, 7*), liquid–liquid extraction (*8, 9*), distillation (*10, 11*), molecular sieve separation (*21*), ion exchange techniques (*12–14*), and chemical methods (*15–20*). The critical review of all these methods has been reported in the literature (*22*). In the present work, an attempt has been made to separate *m*- and *p*-cresols by a sulfonation–desulfonation method.

## EXPERIMENTAL

### Samples and Reagents

An industrial cresol mixture containing 34.3% *m*-cresol, 41.6% *p*-cresol, 4.16% *o*-cresol, and 15.6% phenol, obtained from Rourkela Steel Plant, Rourkela, India, was used. Pure reagent grade 98% $H_2SO_4$ and 99.5% chloroform (British Drug House, India) were used.

### Procedure

The reaction was carried out in a 500-mL round bottom 3-necked glass flask, fitted with stirrer, and arranged in a water/oil bath with temperature controller. $H_2SO_4$ was gradually added to the cresol mixture in the flask at the desired temperature. At the end of each experiment the reaction mass was cooled and diluted with water using 1.5 to 2 times the weight of the reaction mixture. Initially, vacuum distillation of the diluted reacted mass was carried out to remove unreacted components. This procedure took 5–6 h for separation. Next steam distillation was tried, but this procedure also took about the same time to separate unreacted components from the reacted mass. The unreacted components were successfully removed by extraction with chloroform.

The isolated sulfonated *m*-cresol product was desulfonated by hydrolysis. The hydrolysis for the desulfonation was done by heating at 125–130°C. The liberated cresols were again recovered from the hydrolyzed mass by extraction with chloroform.

A 1/4 in. o.d. and 4 m long stainless steel column packed with 60–80 mesh chromosorb W and 8% Bentone 34 + D.C. 200 was used for analysis. An FID detector was used at 180–185°C. Nitrogen was used as a carrier gas with a flow rate of about 40–60 mL/min.

## RESULTS AND DISCUSSION

### Concentration of *m*-Cresol Sulfonate

The variation of concentration of *m*-cresol in the unreacted product as a function of temperature at different reactant ratios of cresol to sulfuric acid and at 4 h of reaction time is plotted in Fig. 1. A similar trend was observed for the reaction studies at 3, 5, and 6 h duration. For most of the

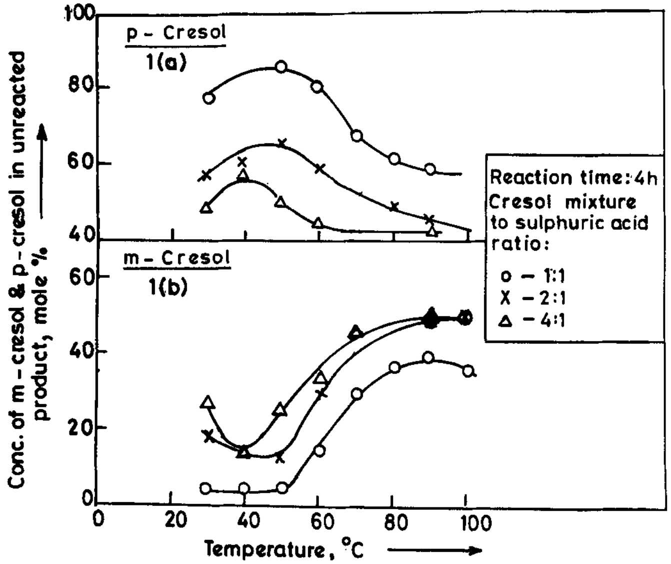

FIG. 1. Concentration of *m*- and *p*-cresol in unreacted product vs temperature of reaction.

conditions studied, a maximum in the concentration–temperature diagram for *m*-cresol sulfonate in the reaction product was observed. It is further observed that this maximum on the concentration–temperature curve shifted in the direction of higher temperature as the feed ratio of the mixture of cresols to $H_2SO_4$ was varied from 4:1 to 1:1 on a weight basis. This shift was more significant after 4 h of reaction time.

## Extent of Conversion of *m*-Cresol

The percent conversion of *m*-cresol to its sulfonate as a function of temperature at different reactant ratios and 4 h reaction time is plotted in Fig. 2, and a similar trend was observed for reaction times of 5 and 6 h.

Figure 2 shows that after an initial increase the conversion drops to a minimum at around 40–70°C and rises again slowly with temperature. A close look at the three curves in Fig. 2 shows that the temperature at which the maximum occurred increased slightly with an increase in the reactant ratio.

The nature of the graphs in Figs. 1 and 2 can be explained on the basis of the rate of sulfonation of other components in the cresol mixture (*p*-cresol, *o*-cresol, phenol) relative to the rate of *m*-cresol sulfonation.

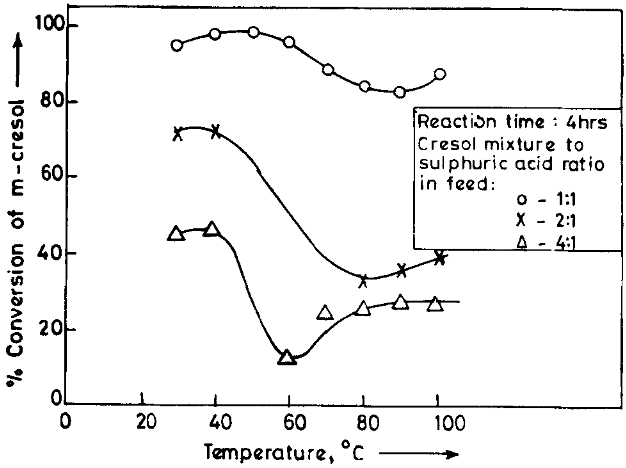

FIG. 2. Percent conversion of *m*-cresol vs temperature of reaction.

TABLE 1

Comparative Velocity Constants of Sulfonation of Phenol, *o*-Cresol, and *p*-Cresol as Compared to *m*-Cresol (*23*)

| Temperature (°C) | *m*-Cresol / *o*-Cresol | *m*-Cresol / Phenol | *m*-Cresol / *p*-Cresol |
|---|---|---|---|
| 20 | 1.872 | 1.395 | 4.823 |
| 40 | 1.662 | 1.362 | 3.013 |
| 60 | 1.339 | 1.118 | 2.230 |
| 80 | 0.495 | 0.399 | 1.563 |
| 100 | — | — | 1.059 |

At lower temperatures (30–40°C), *m*-cresol has a higher rate of sulfonation as compared to *o*-cresol, *p*-cresol, and phenol. Only phenol and *o*-cresol have appreciable rates of sulfonation as compared to *m*-cresol above 80°C. As the temperature is increased, the difference in the rates of sulfonation of *m*-cresol and other impurities continues to diminish as given in Table 1 (*23*).

Therefore, at lower temperatures, i.e., at 30 and 40°C, the ratios of the rate constants of *m*-cresol to *o*-cresol or phenol are significantly large, and hence the overall rate of sulfonation of *m*-cresol becomes large relative to that of phenol, *p*-cresol, and *o*-cresol. As a result of this, at 30 and 40°C there is an increase in concentration of *m*-cresol sulfonate in the reaction product. As the temperature increases beyond 40–50°C, the ratio of the relative rates of reaction of sulfonation of *m*-cresol to *o*-cresol or phenol or *p*-cresol decreases, the decrease being more pronounced in the case of *p*-cresol. At this stage the impurities consume more sulfuric acid in the system and hence the rate of *m*-cresol sulfonation decreases, and the concentration of *m*-cresol sulfonate in the reaction product decreases steadily above 40°C. There is a slow increase in the conversion of *m*-cresol at higher temperatures because the increase in the rate of sulfonation of other impurities at higher temperature is comparatively small (*23*) (Table 1). In other words, the increase in the rate of sulfonation of *m*-cresol is more pronounced at higher temperature compared to the other components in the mixture (phenol, *o*-cresol, *p*-cresol).

## *p*-Cresol to *p*-Cresol Sulfonate

Figure 1 shows the variation of *p*-cresol concentration in the unreacted mixture with temperature for different reactant ratios and reaction times. From these graphs it is clear that the concentration of *p*-cresol sulfonate in the reaction product decreases with temperature (up to 50–60°C) and then increases with a further increase in temperature. This can also be explained as in the preceding section.

The effect of phenol and *o*-cresol in the mixture is more pronounced than *p*-cresol at lower temperatures (50–60°C) because of their higher rates of sulfonation as compared to *p*-cresol. As a result of this, initially the concentration of *p*-cresol sulfonate decreases in the reaction product. Above 50–60°C, the concentration of *p*-cresol sulfonate in the resultant mixture increases because the increase in the rate of sulfonation of *p*-cresol with temperature is considerably higher than for other components (*o*-cresol, phenol) (*23*) (Table 1).

## Sulfonation of Phenol and *o*-Cresol

The variation in the concentration of other impurities in the cresol mixture (phenol + *o*-cresol) with the reaction temperature for a 4-h reaction time and different reactant ratios is shown in Fig. 3.

The trend in Fig. 3 shows that under most of the conditions studied, the concentration of sulfonates of impurities in the reaction product decreases with an increase in temperature in the lower temperature range (30–40°C). It then increases rapidly with an increase in the reaction temperature above 40°C. In some cases (reactant ratios of cresol:sulfuric acid = 1:1 and 2:1, reaction time = 5 h), it is found that the concentration of sulfonates of impurities decreases slightly with an increase in temperature above 80–90°C. The decrease in the concentration of sulfo-

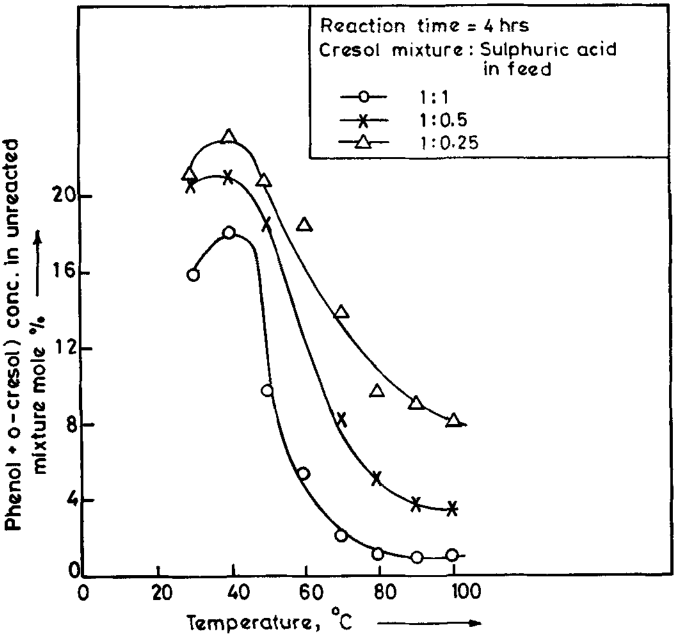

FIG. 3. Concentration of impurities (phenol + *o*-cresol) in unreacted product vs temperature of reaction.

nates of impurities with an increase in temperature in the lower temperature range can be explained as in the earlier cases, with the help of Table 1. The slight decrease in the concentration of the sulfonates of impurities at higher temperatures may be due to hydrolysis of the sulfonates.

## SELECTIVITY

### Effect of Temperature

It may be concluded from the foregoing discussion that the concentration of *m*-cresol sulfonate in the reaction product increases with an increase in temperature in the lower temperature range (30–40°C), while the concentration of sulfonates of other components in the cresol mixture (*p*-cresol, *o*-cresol, phenol) decreases in that temperature range. But as the temperature is further increased, the reverse of the above phenomena occurs. Thus the sulfonation reaction is more selective toward *m*-cresol at lower temperatures.

### Purity of the Product (*m*-Cresol)

Purity of the final product (*m*-cresol) not only depends on the concentration of *m*-cresol sulfonate in the reaction product, but also on the total quantity of *m*-cresol sulfonate. Since all the unreacted product cannot be removed completely, in the cases in which the quantity of *m*-cresol sulfonate is small, even trace amounts of unreacted cresol will very much affect the purity of the final product, even when *m*-cresol sulfonate is present in very high concentration in the reaction product. Hence the product obtained from a reactant ratio of cresol mixture to sulfuric acid as 4:1 will be most susceptible to the impurities and as 1:1 the least. Therefore, a 1:1 reactant ratio gave the maximum purity of *m*-cresol.

## CONCLUSIONS

On the basis of results obtained, the following conclusions can be drawn.

(a) Sulfonation of cresols is a temperature-sensitive reaction, and is selective toward *m*-cresol at lower temperatures.
(b) During the time interval studied, the selectivity of *m*-cresol, compared to *p*-cresol, does not change appreciably with time.
(c) The lower the reactant ratio of cresol mixture to sulfuric acid, the more the selectivity of the sulfonation reaction is toward *m*-cresol sulfonation.
(d) The purity of *m*-cresol obtained in the final product is a function of reaction temperature and time.
(e) The cresol mixture to sulfuric acid ratio of 1:1 gives maximum purity and recovery of *m*-cresol for a fixed reaction temperature and time.
(f) The best conditions are found to be a reaction temperature of 80°C, a time of 4 h, and a reactant ratio of cresol mixture to sulfuric acid of 1:1. Under these conditions, conversion to *m*-cresol sulfonate was 96.5%, and overall recovery was 63% based on *m*-cresol in the original crude cresol mixture. The maximum purity of *m*-cresol obtained was 80%, which can be enhanced to 90% by mere crystallization, or can be enhanced by further sulfonation–desulfonation of the enriched mixture.

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