

Production of *p*-toluenesulfonic acid by sulfonating toluene with gaseous sulfur trioxide

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Abstract: Toluene was sulfonated by gaseous sulfur trioxide to prepare *p*-toluenesulfonic acid. The effects of reaction temperature and toluene conversion on the isomer selectivities and the dynamic viscosity of the reaction mixture in a well-stirred tubular glass reactor of 4 cm diameter and 16 cm height were investigated. Lower selectivity to the *m*-isomer was obtained at lower reaction temperature and lower conversion of toluene, whereas the selectivity to the *p*-isomer seemed to be less affected by these parameters. With the increase in toluene conversion a sharp increase in viscosity of the reaction mixture was observed, which was attributed to the saturation of the toluenesulfonic acids dissolved in toluene. A pilot-scale stainless steel jet loop reactor (JLR) of 0.3 m diameter and 4 m height with an external cooler was constructed and used for the continuous sulfonation of toluene. It was found that the JLR was very effective for the fast removal of the large amount of reaction heat, and selectivities to the *p*-isomer around 85% and to the *m*-isomer below 1.2% were obtained.

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Keywords: toluene; sulfonation; sulfur trioxide; *p*-toluenesulfonic acid; jet loop reactor

NOTATION

C_T	Content of the total toluenesulfonic acids in the reaction mixture (% w/w)
FFR	Falling film reactor
JLR	Jet loop reactor
<i>m</i> -	<i>Meta</i> -
<i>o</i> -	<i>Ortho</i> -
<i>p</i> -	<i>Para</i> -
ν	Dynamic viscosity of reaction mixture (N s m^{-2})

1 INTRODUCTION

p-Toluenesulfonic acid has extensive application in the chemical industry as a catalyst, detergent solubilizer, resin hardener and intermediate for production of many useful chemicals such as *p*-cresol.¹ *p*-Toluenesulfonic acid is industrially produced by sulfonation of toluene with concentrated or fuming sulfuric acid.^{1–4} The processes using sulfuric acid have the disadvantages of high reaction temperature, long reaction time, formation of waste acid due to the production of water, and pollution to the environment. An appropriate method to overcome the above drawbacks is to use sulfur trioxide as the sulfonating agent instead of sulfuric acid. Theoretically speaking, SO_3 is the most efficient sulfonating agent since only direct addition of the SO_3 group is involved and there is no formation of

water during the reaction. Some advantages of using SO_3 include the fast and complete reaction, obviation of waste acid disposal and a minimum environmental impact.^{5,6} Nevertheless, the reaction of SO_3 with alkylbenzenes is highly exothermic (for example, $-1.68 \times 10^5 \text{ J mol}^{-1}$ of SO_3 for the sulfonation of dodecylbenzene) and requires fast removal of the large amount of reaction heat to avoid degradation of the products.⁴ Although the sulfonation of long chain alkylbenzenes such as dodecylbenzene with SO_3 has already been practiced for several decades,^{7–9} the commercial scale sulfonation of toluene with gaseous SO_3 has not been reported until now. Several researchers have reported their investigations on this subject. Sohrabi⁵ studied the kinetics and found that the reaction of toluene with gaseous SO_3 was simultaneous and the overall rate was governed by the diffusion of the two reactants to a reaction plane. Davidsohn⁶ patented a method where the sulfonation reaction was carried out in a successive series of stirred vessel reactors, giving directly *p*-toluenesulfonic acid with a yield of up to 99%. So far, no detailed information is available about the influence of the operational conditions on the isomer distribution and the variation in viscosity of the reaction mixture during reaction, which is very important and useful for the development of a commercial process. Since any commercial sulfonation process can only be conducted at lower viscosity of reaction mixture to evade the

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(Received 12 July 2000; revised version received 4 January 2001; accepted 12 February 2001)

degradation of the heat and mass transfer ability of the reaction system at higher viscosity. Another key problem to be solved is the fast removal of the large amount of reaction heat, which may lead to the sharp increase in reaction temperature and deterioration of the product. Accordingly, choosing a suitable type of sulfonation reactor is an important task.

In this work, the effect of temperature on the sulfonation of toluene with gaseous SO_3 in a bench-scale tubular glass reactor was investigated. A pilot-scale jet loop reactor (JLR) with an external tubular heat exchanger (cooler) was constructed and successfully used for the continuous sulfonation of toluene, giving high selectivity to the *p*-isomer and low selectivity to the *m*-isomer.

2 MATERIALS AND METHODS

2.1 Chemicals

Toluene with a water content below 0.01% (w/w), SO_3 with a purity over 99.99% and nitrogen with a water content below 0.001% (v/v) were commercially obtained. All the other reagents used were of analytical grade.

2.2 Analytical methods

The concentration of SO_3 in the exit gas stream was determined by passing the gas stream through a standard NaOH solution for a predetermined period of time. The excess sodium hydroxide was titrated using hydrochloric acid. The SO_3 concentration was the average of five parallel operations and the error was within $\pm 10\%$. The content of total acids in the sulfonation mixture was obtained by titration with standard alkali solution. The content of free sulfuric acid in the sulfonation mixture was determined by first adding a BaCl_2 – MgCl_2 standard solution to precipitate the SO_4^{2-} as BaSO_4 , then the excess Ba^{2+} was titrated by ethylenediaminetetraacetic acid (EDTA) in

an NH_4OH – NH_4Cl buffer (pH 10) using chrome black T as the indicator. The content of total sulfonic acids was calculated by the difference.

The isomer distribution in the sulfonation product was analyzed by gas chromatography. The product sample was first transformed into their corresponding ethyl esters by reaction with triethyl orthoformate in toluene.¹⁰ Then the treated sample was injected into a gas chromatograph (GC-14A, Shimadzu, Japan). The column (3 mm diameter and 2.9 m length) was packed with white OV-210 on Chromosorb W and maintained at 160°C when in use. Dodecane was used as the internal standard and nitrogen was the carrier gas. The signals were detected by a hydrogen flame ionization detector.

The viscosity of the reaction mixture was detected using a viscometer of Rotovisco RV100 (HAAKE, Germany).

Unless otherwise specified, all of the data are the average of triplicate samples and are reproducible within $\pm 8\%$.

2.3 Experiment in the tubular glass reactor

The effect of temperature on the sulfonation of toluene in a well-jacketed tubular glass reactor of 4 cm diameter and 16 cm height was investigated. A 120 ml aliquot of toluene was added into the reactor and the SO_3 diluted with nitrogen was bubbled into the base of the reactor with stirring at *ca* 500 rpm. The temperature of the reaction mixture was controlled at the predetermined values ($\pm 1^\circ\text{C}$) by deliberately adjusting the flow rates of the gas mixture and the cooling water through the jacket. The concentration of SO_3 in the gas phase was maintained at 7.5% (v/v) throughout the experiments.

2.4 Experiment in the JLR

The schematic diagram of the JLR experimental apparatus is shown in Fig 1. The JLR, made of

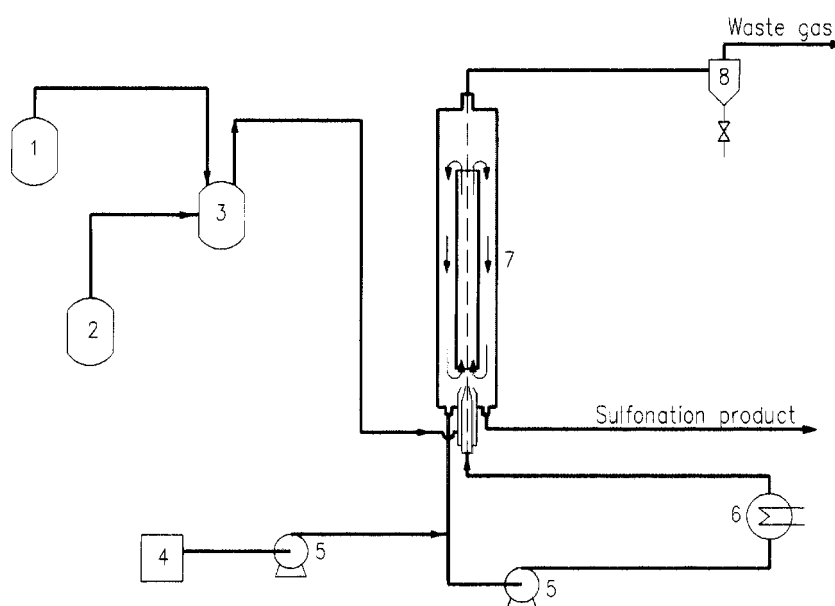


Figure 1. Schematic diagram of the sulfonation apparatus. 1: N_2 reservoir, 2: SO_3 reservoir, 3: gas mixer, 4: toluene reservoir, 5: pump, 6: cooler, 7: jet loop reactor (JLR), 8: cyclone separator.

stainless steel, consisted of an inner draft tube of 0.2 m diameter and 2 m height, an external column of 0.3 m diameter and 4 m height. For fast removal of the large amount of reaction heat, a tubular heat exchanger (cooler) made of stainless steel with an effective heat transfer area of 2.0 m² was externally attached to the JLR. The gaseous SO₃ was prepared by mixing pure SO₃ with nitrogen in a gas mixer. The mixed gas was introduced through the base of the reactor through a ring gas nozzle arranged concentric to the liquid jet. Fresh toluene was continuously pumped and mixed with the recycling reaction mixture, then forced through the external cooler and injected into the reactor through a liquid nozzle at the bottom of the vessel. The waste gas left the JLR from the top and was let out after passing through a cyclone separator. The product stream was continuously withdrawn from the base. The reaction temperature was maintained at 5–10 °C and the SO₃ concentration in the gas phase was kept at 7.5% (v/v).

3 RESULTS AND DISCUSSION

3.1 Effect of reaction temperature on isomer selectivity

The effects of reaction temperature on the selectivities to the *o*-, *m*-, and *p*-toluenesulfonic acids are summarized in Table 1. It is evident from Table 1 that the reaction temperature strongly affected the selectivity to the *m*-isomer, the higher the reaction temperature, the larger the selectivity to the *m*-isomer. The selectivity to the *p*-isomer appeared less affected by the reaction temperature. By statistical analysis the average selectivity to the *p*-isomer was found to be 82.5% with a confidence range of (81.7%, 83.3%) at a confidence level of 95%. So it seems that the effect of increasing reaction temperature was to convert the *o*-isomer to the *m*-isomer without materially affecting the selectivity to the *p*-isomer. It is noted that the

conversion of toluene also affected the selectivities to the *m*- and *o*-isomers but did not obviously influence the selectivity to the *p*-isomer. The higher the toluene conversion, the larger the selectivity to the *m*-isomer. The small amount of *m*-isomer in the sulfonation product is very difficult to isolate from the other two isomers because the *m*-isomer is oily and does not readily crystallize. Therefore, for minimizing the formation of the *m*-isomer and considering the process economy, the reaction temperature between 5 and 10 °C is thought to be appropriate for a commercial-scale operation. It is worth mentioning that for the sulfonation of alkylbenzenes with SO₃ small amounts of sulfones were often formed as by-products.⁵ However, in the bench-scale experiments no detectable formation of sulfones was observed.

3.2 Dynamic viscosity of the reaction mixture

The variation in dynamic viscosity of the reaction mixture with the conversion of toluene is shown in Fig 2. When the conversion of toluene was below 30%, the variation in viscosity was not remarkable. However, an obvious increase in viscosity began when the conversion of toluene was over 30%, and a sharp increase occurred when the conversion of toluene reached a critical value (around 50%), which was dependent on the temperature. The sharp increase in viscosity of the reaction mixture might be attributed to the saturation of the toluenesulfonic acids dissolved in benzene, leading to the severe degradation of the mass and heat transfer ability of the reaction system. Accordingly, in order to make the sulfonation reaction occur smoothly, the conversion of toluene should be maintained at lower level. Considering the feasibility and economy of a commercial-scale operation, the conversion of toluene between 30 and 40% might be appropriate. The toluene conversion of 30% suggested by Davidsohn in his patent⁶ might be based on a similar consideration.

Table 1. Effect of reaction temperature and toluene conversion on the selectivity to *m*-, *o*- and *p*-toluenesulfonic acids at an SO₃ concentration of 7.5% (v/v)

Temperature (°C)	Toluene conversion (%)	Isomer selectivity (%)		
		Meta-	Ortho-	Para-
10	14.4	0.8	18.2	81.0
	41.4	0.8	19.3	79.9
	55.7	1.1	15.7	83.2
	77.3	1.2	16.4	82.4
20	14.2	1.1	17.5	81.4
	38.1	1.1	14.7	84.2
	53.6	1.5	16.7	81.8
	64.9	1.5	17.5	81.0
30	13.4	1.2	17.6	81.2
	16.5	1.2	17.4	81.4
	22.7	1.3	17.0	81.7
	31.5	1.5	14.8	83.7
	41.2	1.7	16.5	81.8

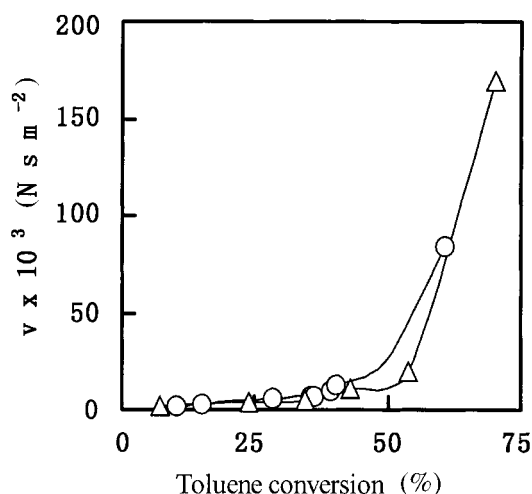


Figure 2. Effect of toluene conversion on the dynamic viscosity of the reaction mixture. SO₃ concentration 7.5% (v/v); temperature: (○) 7.5 °C, (△) 28 °C.

Table 2. Experimental results in the JLR at reaction temperature of 5–10 °C and SO₃ concentration of 7.5% (v/v)

Feed rate of toluene (kg h ⁻¹)	Conversion (%)		Isomer selectivity (%)			C _T (%, w/w)
	Toluene	SO ₃	Ortho-	Meta-	Para-	
10.4	31.6	99.5	13.8	1.2	85.0	46.3
14.4	39.5	99.3	13.6	1.2	85.2	55.1
17.4	38.9	99.2	13.7	1.0	85.3	54.3
19.1	38.1	99.4	13.6	1.1	85.3	53.5

The high sensitivity of the isomer selectivities to the reaction temperature and the simultaneous and strongly exothermic features^{4,5} were the main reasons why we chose a JLR for the sulfonation of toluene rather than the conventional falling film reactor (FFR) as used for the sulfonation of dodecylbenzene. In sulfonation of dodecylbenzene in an FFR, although the reaction temperature is as high as 40–60 °C, the *p*-isomer is formed exclusively. However, if the sulfonation of toluene is conducted in an FFR, as the molecular weight of dodecylbenzene is 2.6-fold that of toluene, at the same liquid flow per wetted perimeter (kgs⁻¹ m⁻¹), the amount of SO₃ needed for toluene is 2.6 times that for dodecylbenzene. Thus, the reaction heat produced is also about 2.6 times that for dodecylbenzene. In sulfonation of toluene, the selectivity to the *m*-isomer increases with the increase of reaction temperature and low selectivity to the *m*-isomer is preferentially considered, so the large amount of reaction heat must be removed simultaneously. However, the very limited gas–liquid interfacial area of an FFR is far from sufficient for the simultaneous removal of so large amount of reaction heat to maintain the required low reaction temperature.^{11,12} In addition, the high vapor pressure of toluene (the boiling point of toluene is *ca* 110 °C while that of dodecylbenzene is *ca* 331 °C) also makes it unsuitable to conduct the sulfonation reaction in an FFR. If so, there would be significant gas phase sulfonation under the inadequate heat exchange conditions, resulting in severe charring. In contrast, in the case of using a JLR,^{13–16} the reaction mixture is well mixed (thus no hot point as that in the FFR) and the large amount of reaction heat can be readily removed by the external cooler. In theory, the heat exchange capacity of the external cooler can be readily adjusted by altering its size.

3.3 Experimental results in the JLR

The experimental results in the JLR are listed in Table 2. It is obvious from Table 2 that under the test conditions, the selectivity to the *m*-isomer was controlled below 1.2%, whereas the selectivity to the *p*-isomer was around 85%, slightly higher than that observed in the bench-scale tubular reactor (82.5%). The conversion of SO₃ was almost complete (over 99%). These results clearly show that the JLR with an external cooler was a very suitable reactor for the continuous sulfonation of toluene by gaseous SO₃ in terms of the low selectivity to the *m*-isomer. It should be mentioned that in the products obtained in the JLR

a small amount of ditolyl sulfone (*c* 1.0%, w/w) was detected. The presence of the small amount of sulfone in the JLR might be responsible for the slightly higher selectivity to the *p*-isomer than that observed in the bench-scale tubular reactor. This observation is consistent with sulfones serving as an orienting agent to direct the formation of the *p*-isomer.⁶

4 CONCLUSIONS

In the sulfonation of toluene with gaseous SO₃, the reaction temperature and conversion of toluene strongly affected the isomer selectivity and viscosity of the reaction mixture. Lower selectivity to the *m*-isomer was observed at lower reaction temperature and lower conversion of toluene, while the selectivity to the *p*-isomer seemed to be less influenced by these parameters. With the increase of toluene conversion a sharp increase in viscosity of the reaction mixture was observed, which was attributed to the saturation of toluenesulfonic acids dissolved in benzene, leading to the severe degradation of the heat and mass transfer ability of the reaction system. Accordingly, for the normal conduction of the sulfonation reaction and the low selectivity to the *m*-isomer, both reaction temperature and toluene conversion should be kept at lower levels.

The continuous sulfonation of toluene by gaseous SO₃ was performed in a pilot-scale jet loop reactor. The fast removal of the large amount of reaction heat was successfully solved by using an external cooler. The reaction temperature was 10 °C and the gaseous SO₃ concentration was 7.5% (v/v), the conversion of toluene was controlled at 30–40%. Selectivities to the *p*-isomer of around 85% and to the *m*-isomer below 1.2% were derived.

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