Mononitration of *m*-Xylene

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The optimum conditions for the mononitration of *m*-xylene must be known, to complete the information on all three xylenes. The meta isomer is available in largest quantities for nitration. A maximum yield of 98% mononitro-*m*-xylene can be secured by nitrating under the following optimum conditions: 1.08 moles of sulfuric acid per mole of xylene, 10% excess nitric acid, sulfuric acid concentration 81%, temperature 30° C., for 60 minutes. Of the three xylenes, the *m*-xylene is nitrated most easily. This is fortunate because it is the isomer not utilized in oxidation processes; hence is available in largest quantities.

TWO previous papers have dealt with the mononitration of *p*-xylene (*11*) and *o*-xylene (*12*). This paper reports the mononitration of *m*-xylene and compares the results found on all three xylene isomers.

All three isomers of xylene are available in commercial quantities as a result of catalytic hydroforming of selected petroleum fractions. The potential production of the xylenes is large and fundamental work on their chemical utilization is of importance. Nitration is one of the important unit processes of organic synthesis; hence the mononitration of the xylenes represents an important step in a study of utilization reactions.

Previous Work

Little work has been done on the nitration of *m*-xylene. Early workers (*3, 6–8*) were concerned with nitration only as an incidental step toward the synthesis of various products and were not particularly interested in yields or in the influence of the process variables. Other workers investigated the effects of mercury or solvents (*10, 14*) on the reaction, but with rather poor results.

Fuming nitric acid was originally used as the nitrating agent, but as early as 1885 Nolting and Forel (*13*) reported results obtained with sulfuric acid–nitric acid mixtures on various xylenes. Yields expected in commercial equipment have been given in patents by Castner (*5*) and Batchelder (*4*), which were reviewed by Kobe and Levin (*11*).

Adams *et al.* (*1*) reported in great detail the process used by the Germans at Leverkusen. In this plant the nitration was carried out with mixed acids over a period of 4.5 hours; the temperature was allowed to rise from an initial temperature of 15° to 35° C. at the end of the reaction. The yield reported was 88% of the theoretical, 25% of this being the 2-nitro-*m*-xylene and 75% the 4-nitro-*m*-xylene, with the dinitroxylene amounting to less than 0.1%. The mixed acid used had a sulfuric acid concentration of 75% on a nitric acid–free basis, with a weight ratio of sulfuric acid to xylene of about 2 to 1. Only 97.5% of the nitric acid theoretically required was charged to the reactor.

Table I. Previous Work

Source	Temp., ° C.	H_2SO_4, %	Theor. HNO_3, %	G. H_2SO_4/G. Xylene	Yield, %	Ratio Mononitro Isomers, 2-, 4-
Batchelder (*4*)	43	79	110	2.19	88	. . .
German industry BIOS report (*1*)	15–35	75	97.5	2	88	25:75
Nolting and Forel (*13*)	0	79	145	1.27	55[a]	. . .

[a] 27% dinitro products also formed.

The data reported by previous workers are summarized in Table I.

Kobe and Levin (*11*) studied the effect of the process variables in the nitration of *p*-xylene using dehydrating value of sulfuric acid (D.V.S.), as a process variable. However, as a result of the work of Haun and Kobe (*9*), it appeared that both the amount and the concentration of the sulfuric acid were more realistic variables. Therefore, Kobe and Pritchett (*12*) used these variables in the investigation of the process variables of the nitration of *o*-xylene, and disregarded the idea of the dehydrating value of sulfuric acid. Both *o*- and *p*-xylene gave a yield of 90% or more mononitro product.

Apparatus and Materials

The nitrator was that used by the two previous investigators; the same steam-distillation apparatus was used with some slight modification so as to increase the rate of recovery.

The *m*-xylene was a technical grade furnished by the Oronite Chemical Co. and was nominally 95% pure. The freezing point reported by Oronite was −49.19° C., corresponding to 96.5% *m*-xylene. As this material was nitrated practically quantitatively and displayed a very narrow boiling range upon distillation,

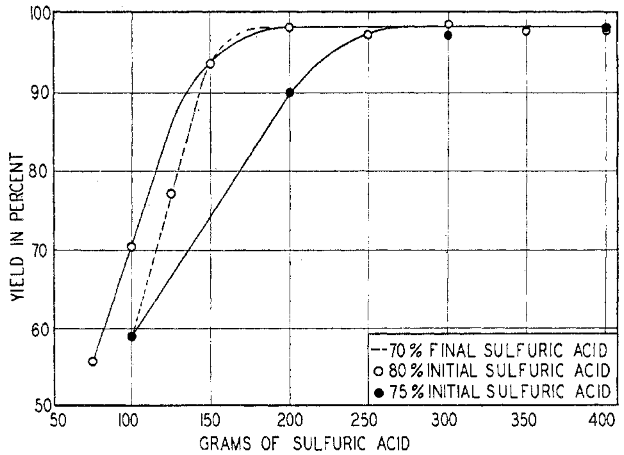

Figure 1. Effect of Amount of Sulfuric Acid on Nitration of *m*-Xylene

200 grams of m-xylene 25° C. nitrated with 10% excess nitric acid, 60-minute addition time

Table II. Experimental Data for Nitration of 200 Grams of *m*-Xylene

Run No.	H_2SO_4, Grams	Concn. of H_2SO_4, %	Temp., ° C.	Excess HNO_3, %	Yield, %	Remarks
1	400	80	25	10	98.0	
2	400	80	15	10	96.9	
4	400	80	10	10	93.6	Some spillage
5	400	80	45	10	92.9	
6	400	70	25	1.6	59.5	
7	400	60	25	1.6	9.2	
8	400	75	25	1.6	80.2	
9	400	80	65	10	32.4	Tar formed
10	400	80	30	10	98.2	
11	400	80	5	10	97.1	
12	400	80	40	10	97.4	
13	400	80	55	10	43.3	Tar formed
14	400	85	25	10	63.7	5% dinitro
15	400	90	25	10	96.5	
16	350	80	25	10	98.0	
17	350	80	35	10	96.8	
18	300	80	25	10	98.9	
19	250	80	25	10	97.4	
20	200	80	25	10	98.2	
21	150	80	25	10	93.8	
22	100	80	25	10	70.4	
23	125	80	25	10	77.1	
24	400	75	45	10	98.4	
25	75	80	25	10	56.1	
27	200	70	25	10	54.4	
28	200	85	25	10	97.5	1% dinitro
29	400	80	50	10	56.2	Tar formed
30	400	75	55	10	97.5	
31	200	75	35	10	90.3	
33	200	75	55	10	96.1	
34	200	80	55	10	48.9	Tar formed
35	400	75	35	10	97.9	
36	200	75	65	10	56.7	Tar formed
37	300	75	25	10	97.5	
38	100	75	25	10	58.7	
39	200	90	25	10	91.2	9% dinitro
40	400	75	65	10	14.1	Tar formed
42	400	75	25	10	98.3	
43	400	60	45	10	34.5	
44	300	75	35	10	95.2	
45	400	70	25	10	92.9	
46	400	60	25	10	19.2	
47	400	60	65	10	57.5	2% dinitro
48	400	75	5	10	71.9	
49	75	80	25	10	58.3	No pot acid
50	200	90	25	10	89.4	No pot acid
51	200	80	25	10	97.5	
52	200	80	25	5	95.9	
55	200	80	25	−5	87.3	
56	200	80	25	−2	92.6	
57	400	60	75	10	78.3	
58	200	80	45	10	97.9	
59	200	75	45	10	94.8	
60	200	75	25	10	90.0	
61	150	75	35	10	84.5	
62	200	80	35	10	93.6	Bad nitric acid
63	400	60	85	10	53.3	Tar formed
64	200	80	25	10	87.4	Time 15 min.
65	200	80	25	10	91.0	Time 30 min.
66	200	80	25	10	93.4	Time 45 min.
67	200	75	35	10	90.0	
68	200	75	15	10	77.7	
69	200	85	35	10	96.0	
70	200	85	15	10	93.0	4% dinitro
71	200	80	15	10	90.5	
72	200	90	15	10	83.5	10% dinitro
73	200	80	25	10	92.0	75% H_2SO_4 in pot
74	200	80	25	10	83.7	All H_2SO_4 in pot
75	200	80	25	10	98.5	No pot acid

Time of reaction is 60 minutes in all runs except 64, 65, and 66 as noted in Remarks.

no attempt was made to purify it and it was considered as 100% pure *m*-xylene in all calculations.

Acids used were all analytical grade; only colorless or pale yellow nitric acids were used in the preparation of the mixed acids.

Method of Nitration

The technique employed was substantially that of Kobe and Pritchett (*12*), with some slight simplifying modifications. In most of the runs 40% of the sulfuric acid was diluted to the desired strength and added to the nitration flask (hereafter referred to as nitrator acid). The remainder of the sulfuric acid, suitably diluted and mixed with nitric acid, was placed in the mixed acid feed buret (hereafter referred to as mixed acid). Two hundred grams of xylene was then weighed out and poured into the nitration flask. This amount was the largest amount that could be contained in the nitrator and be properly emulsified. Immediately after the addition of the xylene the stirrer and the cooling pump were started, and the acid buret was opened to allow the mixed acid to drip in at a steady rate. This acid was added over a period of 1 hour, with the agitation being continued for an additional 15 minutes, at which time the reaction was considered complete. The temperature and amount of acid added were recorded every 5 minutes as an aid in keeping the acid rate and reaction temperature constant.

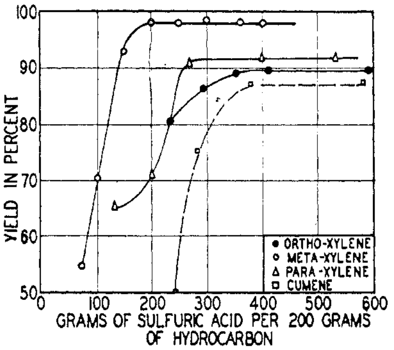

Figure 2. Effect of Amount of Sulfuric Acid on Nitration of Xylenes and Cumene

All acids, water, and hydrocarbon were weighed out to the nearest 0.1 gram on a calibrated, triple-beam laboratory balance. Reactants were cooled only to room temperature before the nitration was begun and no difficulties were encountered. The reaction appeared to start immediately upon the addition of the mixed acid and excellent emulsions were readily obtained. Shortly after the beginning of the reaction the emulsion took on the appearance of tomato soup, in both color and texture.

At the conclusion of each run the entire reaction mass was washed into the steam-distillation flask and diluted to reduce the sulfuric acid concentration to less than 30%. This technique was necessary because in some instances the emulsion formed during the reaction would not break after several hours' standing. Several trials showed that this method caused no complications; it was much more rapid than the method of Kobe and Pritchett and smaller handling losses resulted. The whole mixture was

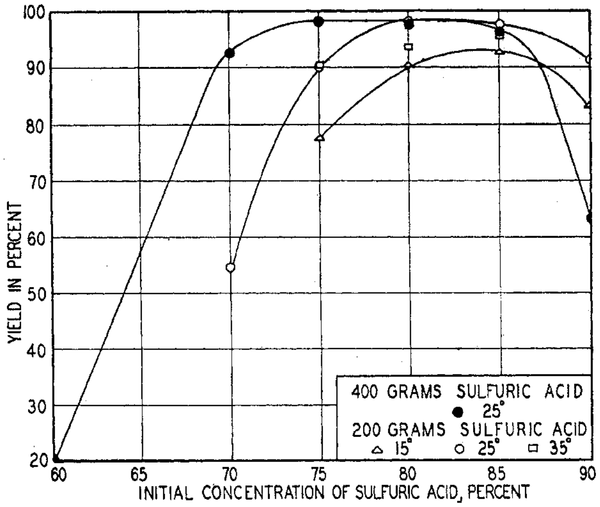

Figure 3. Effect of Acid Concentration on Nitration of *m*-Xylene

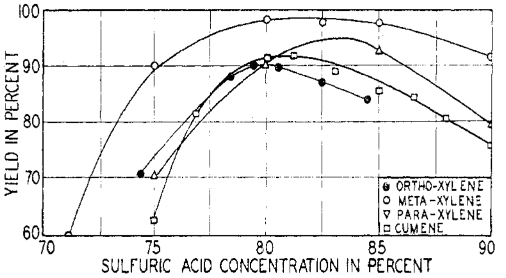

Figure 4. Effect of Sulfuric Acid Concentration on Nitration of Xylenes and Cumene

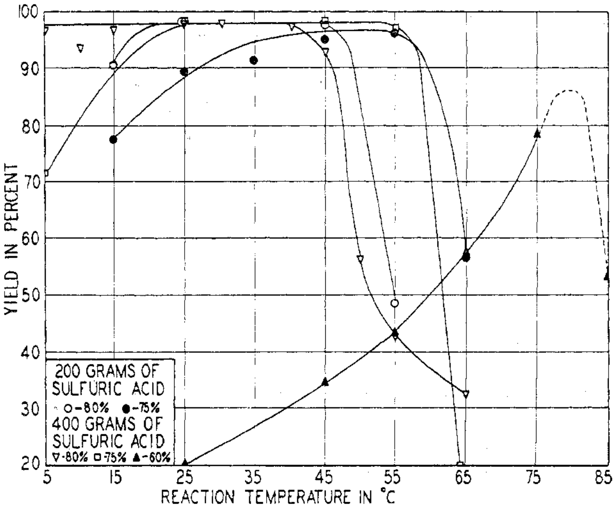

Figure 5. Effect of Temperature on Nitration of *m*-Xylene

then steam distilled and the condensed vapors were passed through a trap. To make the trap effective, it was found necessary to extend the condenser outlet beneath the surface of the liquid in the trap. When the organic phase in the trap began to sink, it was collected and weighed as mononitro-*m*-xylene. Any cloudiness or other water in the sample was removed by passing the liquid through Drierite which had been wet with dry nitroxylene.

Process Variables

Until recently the variables considered in nitration were temperature, dehydrating value of the sulfuric acid (D.V.S.), and nitric ratio (N.R.) The D.V.S. value is related directly to the final sulfuric acid concentration at the end of the reaction, and originated in the idea that the nitration reaction is a simple one between molecular nitric acid and the hydrocarbon and that the sulfuric acid helps bring the reaction to completion by removing the water formed in the reaction. There is ample evidence now that this is not the case; therefore, following the work of Kobe and Pritchett, the dehydrating value of sulfuric acid was disregarded and other process variables were selected.

The process variables studied were the amount and the concentration of sulfuric acid, the time and the temperature of the reaction, the proportion of the sulfuric acid in the mixed acid, and the amount of nitric acid present. Agitation is another important variable, the effect of which was minimized by using a high rate of stirring in all runs, so that the best possible emulsification was always attained. The concentration of sulfuric acid (on a nitric acid–free basis) was always the same in both nitrator acid and mixed acid.

Throughout this investigation the nitration reaction proceeded smoothly with a minimum of side reactions. Many minor factors which could conceivably have affected the yield had no discernible influence. The data for all nitrations are given in Table II.

Sulfuric Acid. The effect of the amount of sulfuric acid at constant initial concentration on the yield of mononitroxylene is shown in Figure 1. It is apparent that the amount needed depends on the acid concentration. At 80% concentration (approximately the optimum concentration) a minimum of 200 grams of acid could be used before the yield began to decrease. At lower concentrations, such as 75%, considerably more acid had to be used to secure the maximum yield.

According to the D.V.S. concept, the yield should remain constant as long as the final concentration, or D.V.S., remains constant. This is not the case, as the yield drops rapidly when less than 200 grams of sulfuric acid are used, despite the fact that the final acid concentration remains at approximately 70% (D.V.S. = 2.33). This shows conclusively that some minimum amount of sulfuric acid must be present to give the maximum yield.

The amounts of sulfuric acid necessary for the nitration of the three isomeric xylenes and cumene are shown in Figure 2 for the optimum concentration of acid. *m*-Xylene requires the least amount of acid, *p*-xylene requires somewhat more, and *o*-xylene and cumene require the most acid. The amount of sulfuric acid required corresponds to the ease of nitration, as would be expected from the orientation of the various isomers. In *m*-xylene the two methyl groups reinforce one another in their activation of the ring, while in *o*- and *p*-xylenes the methyl groups cancel the ring activation to some extent. Since the methyl groups are closer in *o*-xylene, this canceling effect would be expected to be

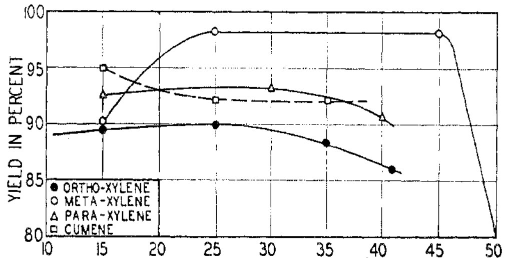

Figure 6. Effect of Temperature on Nitration of Xylenes and Cumene

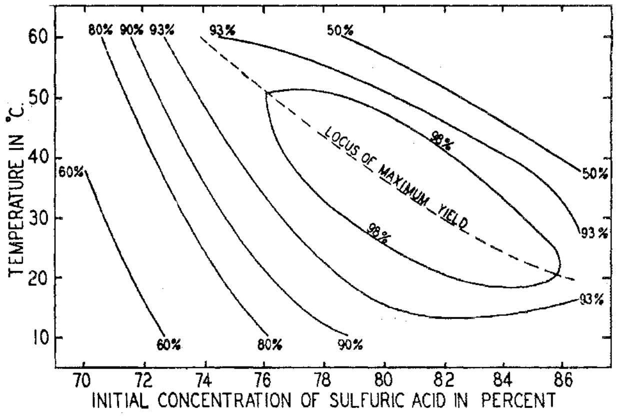

Figure 7. Effect of Temperature and Sulfuric Acid Concentration on Yield of Mononitro-*m*-xylene

stronger, making this the least reactive of the xylenes. In cumene (isopropylbenzene), only one hydrogen is hyperconjugated with the ring, so that its reactivity would be expected to be less than that of *m*-xylene.

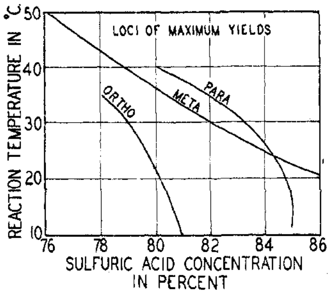

Figure 8. Effect of Temperature and Sulfuric Acid Concentration on Maximum Yield of Mononitroxylenes

Acid Concentration. The acid concentration was varied over a wide range, with the results shown in Figure 3. Using 400 grams of sulfuric acid the peak of the curve is broad and flat; at 200 grams of sulfuric acid, the peak is much sharper, the maximum yield being at approximately 82% initial concentration. The temperature was not critical under these conditions, maximum yield being attained at 25° to 35° C.

Figure 4 illustrates again the relative ease of nitration of *m*-xylene in comparison with the other xylenes and cumene. The peak of the concentration curve is much broader than with the other hydrocarbons, and the yield is considerably higher.

TEMPERATURE. The effect of temperature was determined over a fairly wide range of concentrations and quantities of sulfuric acid. Figure 5 shows that the reaction with *m*-xylene is not sensitive to temperature unless the acid is weak, or unless the temperature passes a certain limiting value. Beyond this limiting value, which is a function of both the amount and concentration of the acid, the yield drops abruptly. This drop in yield is due to the formation of a black, gummy residue, a phenomenon not found in the nitration of the other compounds.

In Figure 6 is shown the effect of temperature on the yield in the nitration of the xylenes and cumene. *m*-Xylene shows the greatest insensitivity to temperature, up to the point where a drastic change occurs.

Kobe and Pritchett (*12*) plotted reaction temperature against acid concentration, with yield as a parameter, as a means of showing how these factors are interrelated. In Figure 7 is shown such a relationship for *m*-xylene. It is seen that a yield of 98% or more of mononitro-*m*-xylene can be obtained within a broad band of reaction conditions.

The lines representing the locus of maximum yield in the mononitration of each of the three xylenes are shown in Figure 8. These curves show the validity of the industrial practice of increasing the temperature of the nitration mixture after a considerable proportion of the mixed acid has been added.

Excess Nitric Acid. Other process variables were held at their optimum values, and the amount of nitric acid was varied from 95 to 110% of its stoichiometric value. The results are shown in Figure 9 and compared with the other xylenes and cumene. It is seen that 10% excess nitric acid is sufficient to give the maximum yield.

TIME OF ADDITION. The time required for the addition of the mixed acid to the nitrator can be varied over a wide range. Limiting factors are the cooling capacity of the nitrator for rapid addition and the production of by-products for slow addition of mixed acid.

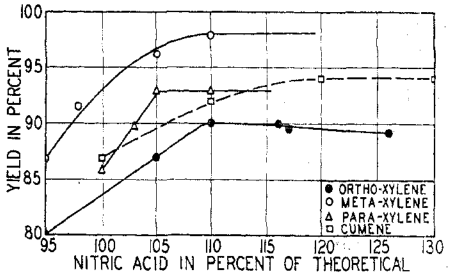

Figure 9. Effect of Amount of Nitric Acid on Yield

If the nitration was continued for the usual 15 minutes after the addition of the mixed acid, within the limits of experimental error the time of addition of the mixed acid had a negligible effect. This was also true for *o*-xylene, as shown by the flatness of the curve in Figure 10, but was certainly not true for *p*-xylene.

In order to get a better representation of the effect of time upon yield, the reaction was quenched with large quantities of cold water immediately after the addition of all the mixed acid. The curve obtained in this manner shows a rather definite maximum at about 60 minutes addition time.

AMOUNT OF SULFURIC ACID IN NITRATOR. For industrial nitrations the practice is to begin the nitration by emulsifying the hydrocarbon with a certain amount of spent acid from a previous nitration. This is not usually done in the laboratory. In order to determine what proportion of the sulfuric acid used should be in the nitrator initially, a series of nitrations was conducted in which the amount was varied from 0 to 100%. The results (Figure 11) show that if less than 50% of the sulfuric acid is in the nitrator initially (the rest is in the mixed acid) the maximum yield can be obtained.

Separation of Isomers

Three isomeric mononitro compounds are possible: the 2-, 4-, and 5-nitro-*m*-xylenes. In the 5-nitro compound the nitro group is meta to the two methyl groups; hence this compound is not found as a product of direct nitration. The physical properties of the three mononitro compounds are given in Table III.

The product from three different nitrations under different reaction conditions was distilled at 80-mm. pressure at high reflux ratio through a

Table III. Physical Properties of Mononitro-*m*-xylenes

Property	2-Nitro-*m*-xylene	4-Nitro-*m*-xylene	5-Nitro-*m*-xylene
Melting point, ° C.	15.3–15.4	8.9–9.0	......
Adams (*2*)	14.8–15.0	8.1–8.3	......
Grevingk (*7*)	......	2	......
Thöl (*16*)	......	......	71
Crystallizing point, ° C.			
Adams (*2*)	14.7	8.05	......
Boiling points, ° C.	220.0 at 740.5 mm.	245.5 at 740 mm.	......
	158.0 at 120.0 mm.	180.4 at 116.5 mm.	......
	147.5 at 86.5 mm.	131.3 at 23.6 mm.	......
	129.5 at 46.2 mm.	......	......
	100.2 at 14.5 mm.	......	......
Grevingk (*7*)	225 at 744 mm.	245.5 at 744 mm.	......
Thöl (*16*)	......	......	255 at 760 mm.
Density, g./cc.	1.112 at 20° C.	1.136 at 20° C.	......
Grevingk (*7*)	1.112 at 15° C.	1.135 at 15° C.	......
Refractive index, n_D	1.5218 at 20° C.	1.5488 at 20.4° C.	......
	1.5199 at 25° C.	1.5471 at 25° C.	......

Table IV. Composition of Steam-Distilled Nitroxylenes Determined by Vacuum Distillation

Components	L[a], %	A[b], %	B[c], %	C[d], %
m-Xylene	...	Negl.	0.9	8.1
2-Nitro-*m*-xylene	...	13.9	13.4	9.5
4-Nitro-*m*-xylene	...	79.9	81.0	79.9
Dinitro-*m*-xylene	0.1	4.1	1.0	Negl.
Loss or tar	...	2.0	3.7	2.5
Ratio of isomers				
2-Nitro	25	14.8	14.2	10.6
4-Nitro	75	85.2	85.8	89.4

[a] Results at Leverkusen plant (*1*).
[b] Distillation of nitration made at optimum conditions with 10% excess nitric acid.
[c] Distillation of nitration made at optimum conditions using 98% of theoretical nitric acid.
[d] Distillation of nitrations made above 50° C. with tar formation.

Table V. Mononitration of Isomeric Xylenes

	Ortho	Meta	Para
Maximum yield, %	90	98	92
Optimum temp., ° C.	25	30	30
Permissible temp. range, ° C.	6-35	5-55	20-40
Moles H_2SO_4/mole xylene	2.22	1.08	2.2
Excess nitric acid required, %	15.8	10	5
Optimum H_2SO_4 concn., %	80	81	85
Permissible H_2SO_4 concn. range, %	78-82	77-85	77-85
Time of reaction, minutes	60	60	30

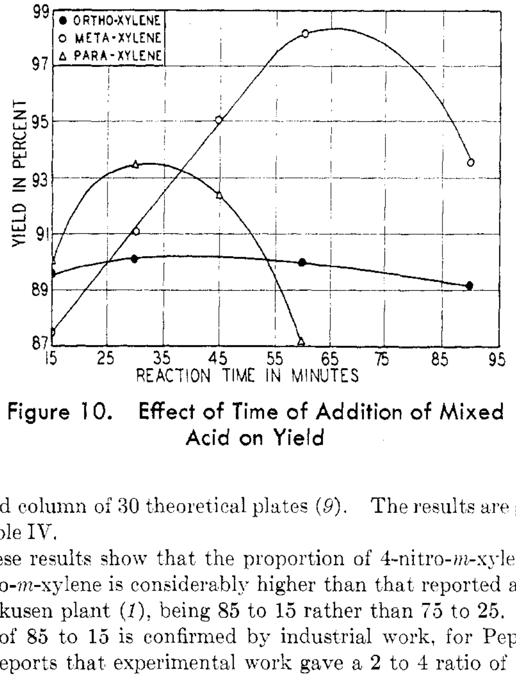

Figure 10. Effect of Time of Addition of Mixed Acid on Yield

packed column of 30 theoretical plates (*9*). The results are given in Table IV.

These results show that the proportion of 4-nitro-*m*-xylene to 2-nitro-*m*-xylene is considerably higher than that reported at the Leverkusen plant (*1*), being 85 to 15 rather than 75 to 25. The ratio of 85 to 15 is confirmed by industrial work, for Peppiatt (*15*) reports that experimental work gave a 2 to 4 ratio of 15 to 85% and Adams and Jones (*2*) found for plant scale operation a 2 to 4 ratio of 16 to 84%. Above 50° C. there is a complete absence of dinitro-*m*-xylene, probably indicating that both it and the 2-nitro-*m*-xylene are preferentially decomposed at higher temperatures.

Comparison of Optimum Conditions

The results of the nitrations of the three xylenes allow a comparison to be made of the optimum conditions for the nitration reaction. Although the results reported for *p*-xylene (*11*) are on the D.V.S. basis, they have been recalculated to the basis of the later work and additional nitrations have been made to allow a comparison with the *o*- and *m*-xylenes. The results are given in Table V.

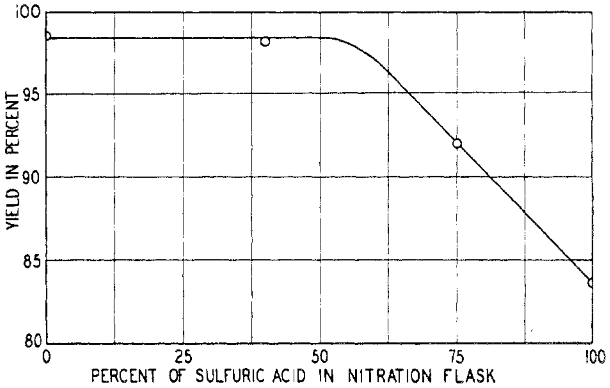

Figure 11. Effect of Initial Distribution of Sulfuric Acid between Nitrator and Mixed Acid

The reaction conditions for maximum yield are roughly equivalent for all three xylenes, with two important exceptions. Higher yields can be obtained from *m*-xylene with half as much sulfuric acid; this shows the ability of the two methyl groups to reinforce one another in their orientation effects. A definite temperature limit exists for *m*-xylene. Above this temperature tar is the main product. For the nitration of mixed xylenes, as carried out during World War II, the nitration conditions should be those required for the compound most difficult to nitrate, the *p*-xylene, which requires the largest amount of sulfuric acid. Because other industrial uses claim large quantities of *o*-xylene for phthalic acid and *p*-xylene for terephthalic acid, the *m*-xylene is the isomer most available for nitration and fortunately is the isomer most easily nitrated.

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END OF ENGINEERING, DESIGN, AND PROCESS DEVELOPMENT SECTION