Dehydrogenation of *p*-Cymene

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An unutilized by-product of the sulfite pulping of spruce, *p*-cymene is also produced by the naval stores industry from terpenes. A dehydrogenation product, *p*,α-dimethylstyrene, could be used in synthetic rubber and polymers.

The dehydrogenation of *p*-cymene to *p*,α-dimethylstyrene was studied over a chrome-alumina catalyst in the temperature ranges 900° F. (482° C.) to 1100° F. (593° C.). Ultimate yields of 80% substituted styrenes can be obtained at a conversion of 50% per pass.

Powers reports that *p*,α-dimethylstyrene copolymerizes with butadiene to give a synthetic rubber superior to GR-S in tensile strength and resembling natural rubber in characteristics. Useful polymers of *p*,α-dimethylstyrene have been reported. The production of *p*,α-dimethylstyrene will give an outlet for *p*-cymene now being sent to waste by sulfite pulp mills.

A READILY available aromatic hydrocarbon, *p*-cymene (*p*-isopropyltoluene), referred to as spruce turpentine in the wood pulp industry, occurs as a by-product of the sulfite pulping of eastern spruce. Frequently, the *p*-cymene is not recovered because of the lack of demand for it, although a large quantity is potentially available. The recent patent literature reports a number of processes by which it can be prepared from monocyclic and bicyclic terpenes (*4, 13*).

Many suggestions have been made for the chemical utilization of *p*-cymene, most of them involving the synthesis of the phenolic compounds carvacrol and thymol. Some of the previous papers in this series have applied the unit processes of nitration (*8, 14*), reduction (*15*), and mercuration (*7, 19*) to produce chemical intermediates. Dealkylation of *p*-cymene to produce toluene was practiced extensively during World War I, at which time recovery equipment was installed in most spruce sulfite mills.

Because of the large market for styrene-type plastics the dehydrogenation of *p*-cymene to *p*,α-dimethylstyrene could become a process which might use chemically a far larger volume of *p*-cymene than used by other chemical processes. *p*,α-Dimethylstyrene is a logical starting material for the synthesis of dimethyltolylcarbinol for use as such or as an intermediate in the synthesis of other aromatic compounds (*21*). For these reasons a study has been made of the dehydrogenation of *p*-cymene.

DIMETHYLSTYRENE

p,α-Dimethylstyrene used previously has been prepared (*5*) by passing vapors of α-pinene, menthane, and other terpenes over a metal oxide catalyst at 600° to 700° C. The α-pinene is isomerized to dipentene which is dehydrogenated to *p*,α-dimethylstyrene. Yields are reported to be relatively low and considerable amounts of *p*-cymene are also produced. Methane can be split from *p*,α-dimethylstyrene to give *p*-methylstyrene (*6*).

p,α-Dimethylstyrene is unlike styrene in that it is not thermally polymerized itself (*21*) but will copolymerize with vinyl compounds to form colorless resins (*22*). In this respect it is similar to α-methylstyrene which is produced commercially (*1, 9*). The patent literature in the last 2 years has shown a considerable number of patents on the polymerization of *p*,α-dimethylstyrene to dimers and trimers, both liquids and solids, for which various uses are proposed.

Of greatest interest is the copolymerization of *p*,α-dimethylstyrene with other unsaturated compounds. Powers (*23, 25*) reports a series of synthetic rubbers made by copolymerization of *p*-α-dimethylstyrene with butadiene. The properties of the copolymer were superior to the styrene copolymers in tensile strength and more nearly resemble natural rubber in processing characteristics.

DEHYDROGENATION

The only work reported on the dehydrogenation of *p*-cymene to *p*,α-dimethylstyrene is by Balandin *et al.* in a Russian article and patent (*2, 3*). They recommended their styrene catalyst and the reduction of the partial pressure of *p*-cymene by adding 2 moles of carbon dioxide per mole of *p*-cymene. Under these conditions the optimum yield was reported as 62.3%. The article mentions an optimum temperature of 625° C., but the patent states 500° C.

Other work has been done on the catalytic dehydrogenation of the isopropyl group in cumene (isopropylbenzene). Nickels *et al.* (*20*) report the catalytic dehydrogenation of cumene at 600° to 650° C. over four catalysts in the absence and presence of steam. The average α-methylstyrene production per pass was 43%, with an ultimate yield of α-methylstyrene and styrene of 71% and 10%, respectively.

Process variables that enter into the dehydrogenation reaction have been investigated most extensively for the dehydrogenation of ethylbenzene to styrene. Temperature should be kept as low as possible, consistent with adequate reaction rates. High temperatures favor dealkylation reactions so that considerable quantities of the reactant are converted to benzene and toluene. Pressure should be kept low to favor a reaction which gives an increase in the number of moles of product. Rather than operate at subatmospheric pressure a diluent is used, such as steam, carbon dioxide, nitrogen, or methane. Steam is usually used, and in the Dow styrene process (*18*) the ratio of 2.6 pounds of steam per pound of ethylbenzene reduces the partial pressure of reaction products to about 0.1 mm. of mercury. Steam also reacts with carbon deposited on the catalyst so the process can operate continuously. By superheating the steam so it will supply the heat of dehydrogenation and mixing it with the ethylbenzene the latter need not be heated directly in a furnace in which carbon deposition would occur. This is satisfactory when an iron oxide on magnesia catalyst is used. However, on a chromium oxide–on–alumina catalyst steam markedly inhibits the dehydrogenation reaction. Benzene has been used as a diluent and heat carrier for the reaction (*16, 17*) using a Universal Oil Products dehydrogenation catalyst. Benzene has the advantage of having a much greater molal heat capacity than steam. It can be separated easily from the unreacted material and reaction products.

DEFINITION OF TERMS

The following terms are used to describe the operating conditions and results obtained.

Liquid hourly space velocity, L.H.S.V., and frequently called simply space velocity, is defined as the volume of liquid feed per hour per gross volume of catalyst zone, as milliliters of *p*-cymene per hour per milliliter of catalyst.

A weight basis is used to express conversion and yields. The molecular weight of *p*-cymene is 134.2 and dehydrogenation reduces it to 132.2 for *p*,α-dimethylstyrene, hence the use of weight

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percentage differs but little from mole percentage in calculating yields.

Yield per pass is the grams of the substituted styrenes produced per 100 grams of *p*-cymene fed to the reactor. It is usually called yield in this paper.

Conversion is the grams of *p*-cymene unrecovered per 100 grams of *p*-cymene fed to the reactor.

Ultimate yield is the grams of substituted styrenes produced per 100 grams of *p*-cymene unrecovered—i.e.,

$$(\text{yield})(100)/(\text{conversion})$$

EXPERIMENTAL

Dehydrogenation Unit. The laboratory scale dehydrogenation unit consisted of a 1-inch stainless steel pipe, 22 inches long, to one end of which was welded a $^1/_2$-inch stainless steel pipe 14 inches long. A mild steel block 4 inches in diameter and 25 inches long was drilled to contain the 22-inch catalyst tube and 3 inches of the $^1/_2$-inch pipe. The steel block was surrounded by a grooved ceramic sleeve which was an electrical insulator for two 1250-watt heaters wrapped in parallel. The block was insulated with 5 inches of 85% magnesia and enclosed in a cylindrical sheet-metal shell. The temperature of the block was controlled by a Wheelco Capacitrol controller, usually at a temperature about 5° to 15° F. above the desired hydrocarbon temperature. A thermocouple well of $^3/_8$-inch stainless steel tubing projected upwards through the $^1/_2$-inch pipe to the catalyst support plate and measured the temperature of the gases leaving the catalyst bed. A similar thermocouple well projected downward 14 inches in the 1-inch pipe and measured the temperature of the gases entering the catalyst bed. Two $^3/_8$-inch holes were drilled $1^1/_8$ inches into the steel block and thermocouples measured the temperature of the block at points corresponding to the top and bottom of the catalyst bed. These four positions are indicated on Figure 1.

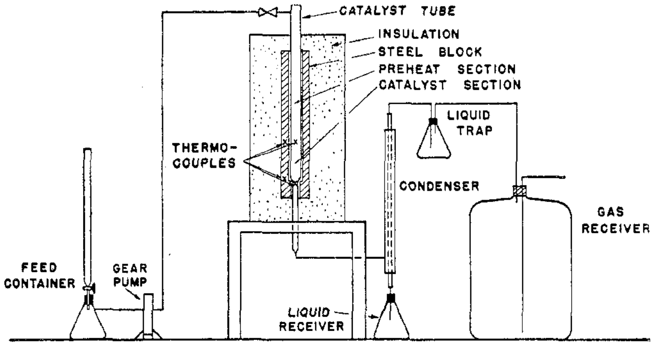

Figure 1. Assembled Dehydrogenation Unit

The catalyst support consisted of a stainless steel plate drilled with $^1/_{16}$-inch holes. The plate rested on the shoulder formed where the 1-inch and $^1/_2$-inch pipes were welded together. For those experiments in which *p*-cymene alone was used as the feed, 100 ml. of catalyst were used; for those in which a diluent was used with *p*-cymene, 50 ml. of catalyst were sufficient. The upper section of the 1-inch tube was filled with $^1/_4$-inch Berl saddles and served as a preheating section.

The feed was delivered at a constant rate from a buret to a flask, from which it was pumped by a Zenith gear pump to the preheat section of the catalyst tube. The effluent from the catalyst tube passed to a condenser where the liquid and noncondensable gases were separated. The gaseous products were collected over a saturated salt solution.

Chemicals Used. The *p*-cymene was supplied by Newport Industries, Inc. It was purified by six acid treatments with 5% of its volume of sulfuric acid, followed by eight washings with water and then was dried over Drierite for 24 hours. It was distilled through a packed 4-foot column and a center cut was taken boiling at 177° to 178° C. The benzene used was commercial grade purified by fractionation to give a boiling point of 80° C.

Catalyst. The catalyst used for this work was a chrome-alumina type catalyst designated by Universal Oil Products Co. as type J-2 dehydrogenation catalyst. It was first prepared by Grosse, Morrell, and Mattox (*12*) and has been used in other investigations (*11*). The catalyst was in the form of cylindrical pellets, $^1/_8$ by $^1/_8$ inch. A fresh batch of catalyst was used for each experiment to eliminate any effect of catalyst poisons.

Procedure. The duration of each process cycle should be sufficiently long to allow a representative test and to obtain sufficient product for analysis. Previous workers with chrome-alumina catalysts have usually used a $^1/_2$- or 1-hour process period because carbon deposition makes a longer test period undesirable. In this work a 1-hour process period was used in order to have sufficient product when low flow rates were used.

In starting a new experiment the block and catalyst tube were heated to the reaction temperature and allowed to remain at that temperature for at least $^1/_2$ hour. Before the feed was introduced the system was thoroughly flushed out with carbon dioxide to remove air. The feed was allowed to flow through the system for 1 hour, after which the system was again flushed with carbon dioxide (which was not allowed to enter the vapor receiver).

ANALYTICAL METHODS

All analyses except the fractionations were run in duplicate to decrease the probability of erroneous results. If duplicate values did not agree within the limits claimed by the originators of the procedure another pair of samples was analyzed. Average values were reported in all cases.

Liquid Product. The liquid product was fractionated in a glass column ($^1/_2$-inch diameter by 2 feet long, packed with $^1/_4$-inch glass helices and using a reflux ratio of 10 to 1) into two fractions. The first fraction contained all material boiling below 145° C. and was small in volume in those runs in which benzene was not used. It averaged about 5%, and under the most severe conditions amounted to only 13% of the liquid product. The initial overhead temperature was about 70° C. and there was no indication of a plateau in the range 70° to 145° C. The bromine number (*24*) of this fraction averaged between 7 and 8. Since this is relatively small and the liquid fraction itself was but a small percentage of the total, this unsaturation was considered to be due entirely to *p*,α-dimethylstyrene which amounted to 6 to 7% of the fraction. *p*,α-Dimethylstyrene has a normal boiling point of 186° C., slightly above that of the *p*-cymene at 177° C. The approximate amount of unreacted *p*-cymene in this first fraction was calculated by multiplying the percentage of *p*,α-dimethylstyrene in the first fraction by the ratio of *p*-cymene to *p*,α-dimethylstyrene in the second fraction.

The second fraction contained all material boiling above 145° C. The bromine number was determined and the result calculated to *p*,α-dimethylstyrene. Several determinations were

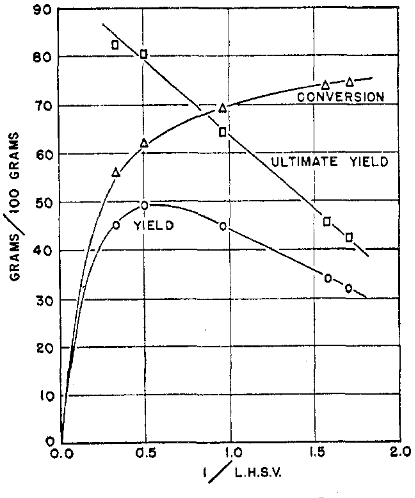

Figure 2. Effect of Space Velocity on Yield, Conversion, and Ultimate Yield at 1100° F.

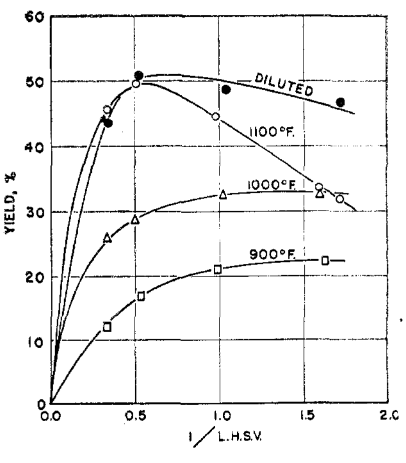

Figure 3. Effect of Temperature and Space Velocity on Yield

Table I. Experimental Data and Results

Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Av. temp., hydrocarbon, ° F.	902	899	903	899	996	998	997	996	1102	1100	1096	1098	1100	1098	1099	1098	1097
Feed[a]																	
Space velocity (L.H.S.V.)	0.62	1.03	1.91	3.15	0.63	0.99	2.04	3.01	0.58	0.63	1.03	2.01	3.05	0.58	0.96	1.97	2.97
1/L.H.S.V.	1.61	0.97	0.52	0.32	1.59	1.01	0.49	0.33	1.71	1.58	0.97	0.50	0.33	1.72	1.04	0.51	0.34
Wt. *p*-cymene fed, grams	52.9	87.7	163	268	53.6	83.8	174	256	49.9	53.4	87.7	171	260	24.4	40.3	82.5	125
Analyses, wt., grams																	
Liquid effluent																	
Fraction No. 1[b]	2.9	3.1	3.0	4.8	2.6	4.7	4.4	10.8	3.1	4.8	4.9	2.7	6.5	..	46.2	90.1	135
Fraction No. 2	46.6	79.2	153.7	254	42.1	69.4	161	229	27.7	32.0	68.7	154	229	19.9	29.9	74.3	118
Vapor	1.2	1.1	1.5	1.5	2.6	2.5	3.4	5.1	5.0	4.9	6.0	7.3	8.0	2.9	3.9	6.2	8.3
Coke	1.7	1.4	1.0	1.5	4.6	4.4	3.8	3.7	11.1	9.6	9.0	7.1	8.1	3.5	4.5	4.3	4.0
Material balance, total, %	98.9	96.7	97.7	97.7	97.1	96.5	99.0	97.2	93.8	96.1	101.1	100.3	96.8	96.8	97.0	98.1	98.7
Production data[c]																	
Total wt. styrenes, grams	11.8	18.9	27.5	32.1	17.4	27.3	50.3	67.0	15.9	18.1	39.2	84.8	118.8	11.4	19.7	42.2	54.7
Recovered *p*-cymene, grams	35.5	64.9	131.0	230.0	25.3	44.1	111.2	170.0	12.7	14.0	27.0	65.3	114.8	..	10.5	33.1	65.3
Yield, wt. %	22.3	21.2	16.9	12.0	32.7	32.6	28.9	26.1	31.8	33.8	44.7	49.6	45.7	46.8	48.8	51.2	43.9
Conversion, wt. %	32.7	27.4	19.7	14.2	52.7	47.4	36.1	33.8	74.5	73.8	69.3	61.7	55.7	..	73.9	60.0	47.6
Ultimate yield, wt. %	68.2	77.3	85.8	84.6	62.1	68.8	80.2	77.2	42.7	45.8	64.5	80.2	82.0	..	66.1	85.3	92.3

[a] Runs 1–13, *p*-cymene undiluted; runs 14–17, 1 mole *p*-cymene + 2 moles benzene. Space velocity based on *p*-cymene only.
[b] Fraction boiling below 145° C.
[c] Corrected to 100% material balance.

made in which the substituted styrenes were determined separately by the method of Elliot and Cook (*10*) with a maximum variation in duplicate samples of 0.7%. Only in runs 14 and 15 was there a definite indication of *p*-methylstyrene, which was less than 10% of the total unsaturation.

Condensed products were determined by evaporating a weighed sample at 100° C. and 5 mm. absolute pressure until successive weighings at 15-minute intervals agreed within 0.2%. The material not reacting with bromine and not left as a condensed product was considered to be unreacted *p*-cymene.

Carbon on Catalyst. The carbon deposited on the catalyst was determined by igniting a weighed sample of catalyst to constant weight.

Gaseous Products. The gas collected in the bottle should be essentially hydrogen with small amounts of methane, propylene, and other thermal decomposition products. The specific gravity of the gas was determined by weighing a sample in a gas balloon.

Material Balances. A material balance was made on each experiment and found to account for 96 to 98% of the incoming material. The lowest value of 94% was on an experiment at very low space velocity.

EFFECT OF PROCESS VARIABLES

The data for the seventeen experiments are given in Table I.

Effect of Temperature and Space Velocity. The space velocity was varied at three temperature levels: 900° F. (482° C.), 1000° F. (538° C.), 1100° F. (593° C.). In Figure 2 is shown the effect of space velocity on yield per pass at 1100° F. The yield per pass has a maximum value of approximately 50% at a space velocity of 2.0.

A comparison of the effect of space velocity on yield per pass (Figure 3), conversion (Figure 4), and ultimate yield (Figure 5) at 900°, 1000°, and 1100° F. is shown graphically. At a given velocity the yield increases markedly with temperature. At 900° and 1000° F. the yield remains practically constant at low space velocities (values of 1/L.H.S.V. above 1.0), but at 1100° F. the longer retention time causes complete decomposition of the feed on the catalyst to give carbon and gases. As space velocity increases the yield passes through a maximum value and then decreases as insufficient contact time is allowed. The conversion, which represents *p*-cymene unrecovered, increases with temperature and with retention time, though the conversion at 1100° F. and low space velocities is to carbon and gas. Ultimate yields decrease with increasing temperature and retention time due to this complete decomposition. An ultimate yield of approximately 80% *p*,α-dimethylstyrene is obtained at 1/L.H.S.V. of 0.5 at either 1100° or 1000° F., but at 1100° F. the yield per pass is 50% compared to 30% at 1000° F.

Effect of Diluent. To determine the effect of diluting the *p*-cymene with benzene, a temperature of 1100° F. was selected because the ultimate yield is higher for a given conversion (Figure 6).

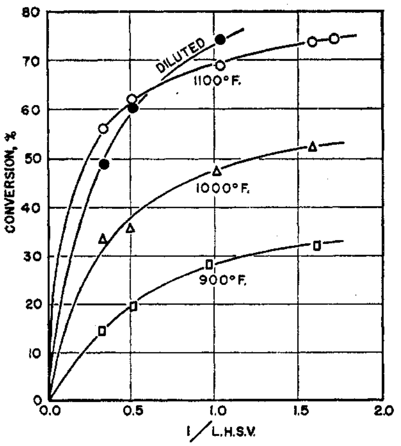

Figure 4. Effect of Temperature and Space Velocity on Conversion

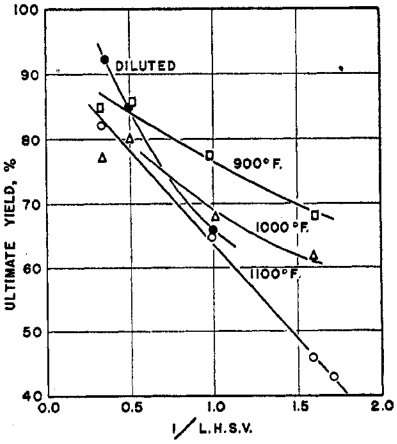

Figure 5. Effect of Temperature and Space Velocity on Ultimate Yield

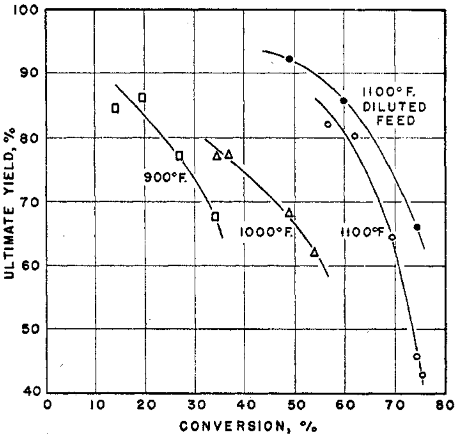

Figure 6. Variation of Ultimate Yield with Conversion of *p*-Cymene

A ratio of 2 moles of benzene to 1 mole of *p*-cymene was used, corresponding to a partial pressure of *p*-cymene in the reactants of approximately 5 pounds per square inch absolute. The yield, conversion, and ultimate yield are shown on Figures 3, 4, and 5 as the curve through the solid points labeled "diluted." It is seen in Figure 3 that the maximum yield per pass is increased only slightly, but at lower space velocities the benzene protects the *p*-cymene from total decomposition and increases the yield of *p,α*-dimethylstyrene. The ultimate yield for a given conversion has increased by about 5%. Mavity *et al.* (*16, 17*) obtained the same type of curves in the dehydrogenation of ethylbenzene using benzene as a diluent.

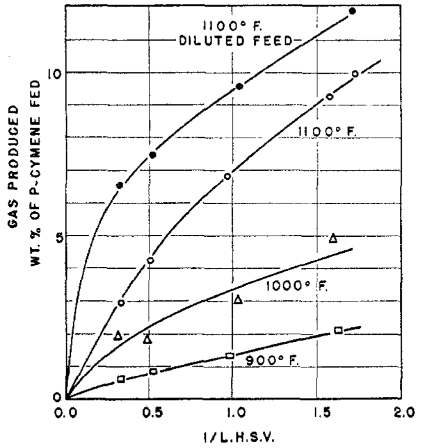

Figure 7. Gas Formation

CONVERSION AND ULTIMATE YIELD. With any dehydrogenation catalyst a wide range of both conversion and ultimate yield can be obtained depending on the operating conditions chosen. Low conversions will give high ultimate yields at the expense of a large amount of recycled feed. In Figure 6 are shown the experimental relationships between ultimate yield and conversion; from these data an economic balance could be made for a given installation to determine the optimum operating conditions. Although a feed diluted with benzene gives a higher ultimate yield, the necessity of distilling 2 moles of benzene per mole of feed must be considered.

GAS FORMATION. The weight of gas formed varied from less than 1% of the feed under mild conditions to about 10% under severe conditions (Figure 7). The diluted feed produced considerably more gas. Mavity *et al.* (*16, 17*) showed that at 1112° F. (600° C.) decomposition of benzene was slight.

CARBON FORMATION. The amount of carbon deposited on the catalyst increases rapidly with increasing temperature and time of contact with the catalyst. Dilution with benzene reduces carbon but little. The relationship between carbon deposition, conversion, and temperature is shown in Figure 8. The temperature of 1100° F. is again seen to be the preferred temperature, as the weight of carbon deposited per unit weight of product is less at a given conversion. Dilution of the feed results in somewhat higher carbon deposition than the undiluted feed at lower conversion levels.

COMPARISON WITH CUMENE. Nickels *et al.* (*20*) report an 89% ultimate yield of styrenes at a conversion of 20% per pass at 112° F. (600° C.) and in a test run at 1157° F. (625° C.) an ultimate yield of 81% styrenes at an average conversion of 43%. It can be seen from Figure 6 that higher ultimate yields at higher conversions per pass can be secured with *p*-cymene.

CONCLUSIONS

p-Cymene can be dehydrogenated over a chrome-alumina catalyst to give essentially *p,α*-dimethylstyrene, but some *p*-methylstyrene is produced.

A temperature of 1100° F. (593° C.) gave higher ultimate yields at any given conversion that the lower temperatures studied.

Dilution of the feed with benzene offers some advantage in giving a somewhat higher ultimate yield at a given conversion than does *p*-cymene alone.

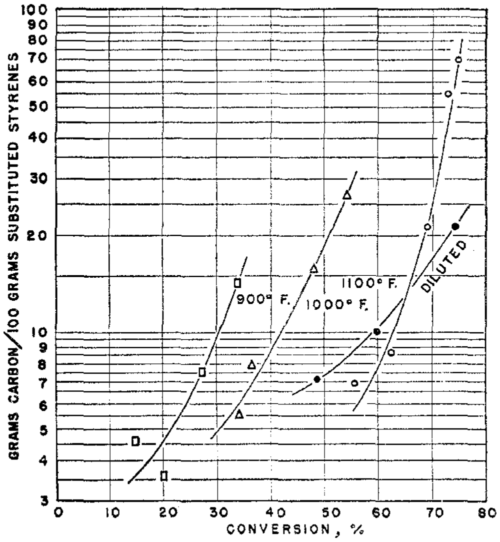

Figure 8. Relationship between Carbon Deposition and Conversion at Various Temperatures

Depropylation and coke formations are not excessive under the proper conditions. Ultimate yields of 80% substituted styrenes can be obtained at a conversion of 50% per pass.

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