BRIQUETS,	and Cor	Œ		,
(Dry h	asis)			
Coals and Raw Briquets	Volatile Matter	Furnace Coke	Ash	Sul- fur
Geneva coal Castlegate coal Geneva coal, tar-bound raw briquet	$\begin{array}{r} 41.0\\ 42.9\\ 38.0\end{array}$	$52.6 \\ 50.5 \\ 55.0$	$ \begin{array}{c} 6.4 \\ 6.6 \\ 7.0 \end{array} $	$0.80 \\ 0.40 \\ 0.46$
Geneva coal, pitch-bound raw bri- quet Geneva coal, curbay-bound raw bri-	37.4	55.9	6.7	0.51

TABLE VII. AVERAGE PROXIMATE ANALYSES OF COALS, RAW

Geneva coal	41.0	52,0	0,4	0.80
Castlegate coal	42.9	50.5	6.6	0.40
Geneva coal, tar-bound raw briquet	38.0	55.0	7.0	0.46
Geneva coal, pitch-bound raw bri-	37.4	55.9	6.7	0.51
Geneva coal, curbay-bound raw bri-			•••	
quet	38.7	54.0	7.3	0.45
Castlegate coal, tar-bound raw bri-	43 8	50 0	62	0.20
Castlegate coal, nitch-hound raw	10.0	00.0	0.2	0.20
briquet	41.1	52.4	6.5	0.21
Geneva tar-bound briquet, carbon-	12	86.8	12 0	0.84
Geneva pitch-bound briquet, car-	1.2	0010	12.0	0.01
bonized at 600° C.	10.9	79.6	9,5	0.40
Geneva pitch-bound briquet, car- bonized at 1000° C.	6.1	83.3	10.6	0.34
Geneva curbay-bound briquet, car-				
bonized at 1000° C.	10.5	75.6	13.9	0.39
Castlegate pitch-bound briquet car-	~ -		10.0	0.00
bonized at 800° C.	2.7	86,4	10.8	0.26

ing economics of coke manufacture. The additional cost of fine grinding and briquetting, as compared with the relatively coarse grinding required for by-product coking, might thereby be compensated.

The most important items to be explored in continued investigation of these methods of coking would be: the maximum practical sizes for the briquets; in the case of the continuous vertical retort, the maximum temperatures attainable, and the maximum feasible retort diameter; in the case of the sole-heated oven, the feasibility of pushing the charge, the maximum dimensions of the oven, and the feasibility of establishing a floor heating and cooling cycle alternating with direct heating in the top of the oven by introduction of air as in beehive oven practice; and the blending of poor coking coals with small amounts of good coking coals, and the blending of coke breeze with the better coking coals. Basket tests on the sole-heated oven runs indicated qualitatively

that coke breeze to the extent of 25 parts breeze to 75 parts of Geneva coal produced strong coke briquets.

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Dehydrogenation of Isopropylbenzene to Alpha-Methylstyrene

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Isopropylbenzene can be catalytically dehydrogenated to α -methylstyrene at 600° to 650° C. in the absence and presence of diluent steam. Catalytic dehydrogenation is superior to noncatalytic dehydrogenation with respect to selectivity, conversion per pass, and ultimate yield. In a 216-hour catalytic run the average α -methylstyrene production per pass was 43%; the ultimate yields of α -methylstyrene and styrene were 71 and 10%, respectively, and the hydrogen content of the exit gas was 96 mole %.

LPHA-methylstyrene, obtainable from isopropylbenzene by dehydrogenation, is a potentially valuable homolog of styrene (1). This paper describes experiments on the catalytic and noncatalytic dehydrogenation of isopropylbenzene with and without diluent steam. A contact time of 0.7 second was employed in all experiments so as to have a common basis of comparison; 0.7 second was an effective contact time for the catalytic dehydrogenation. The only previous information on this reaction is that furnished by patents (3, 4, 5). Isopropylbenzene, because of its ease of preparation, has been considered as a source of styrene. According to the available data this possibility is not promising. Catalytic dehydrogenation is selective for the production of α -methylstyrene. Noncatalytic dehydrogenation of isopropylbenzene at 700° C. can be made to produce mainly styrene at a commercially acceptable rate, but at this temperature the ultimate yield of styrene is less than 60% as compared with the 88% yield obtained catalytically from ethylbenzene.

APPARATUS, PROCEDURE, AND FEED STOCK

The apparatus and procedure were similar to that previously described (6), except for the following details. The reactors

were of Vycor, 19 mm. inside diameter for the experiments with steam and 13 mm. inside diameter for those without steam. The catalyst charges for the runs with and without steam were 40 and 10 cc., respectively. The vaporizer-preheater was an integral part of the reactor, and it was packed with Vycor chips, 4 to 8 mesh for the 19-mm. tubes and 8 to 16 mesh for the 13-mm. tubes, respectively; for the noncatalytic experiments, both the preheater and the reactor zones were packed with Vycor chips.

The catalyst temperatures listed in the experimental data were those recorded by a thermocouple which extended down through the preheater packing (internal thermocouple well) to the top of the catalyst bed. These temperatures did not differ by more than 3° C. from the temperatures at any point within the catalyst bed. In one long experiment (216 hours), the reactor was a 2inch diameter copper-lined steel tube (catalyst charge, 1000 cc.) equipped with a 1500-cc. integral vaporizer-preheater packed with brass jack chain.

The constants of the isopropylbenzene were: boiling point 152° to 153° C. (760 mm.), $n_{\rm D}^{20}$ 1.4915, d_4^{20} 0.862.



ANALYSIS

In general, the product from each 2-hour period was analyzed, and the analytical data in Tables I and II are the averaged values. The liquid products (inhibited by 0.3% of *p*-tert-butylcatechol) were distilled at 50 mm. through a 43-plate packed glass column, removing benzene, toluene, ethylbenzene, styrene, and part of the isopropylbenzene overhead and leaving α -methylstyrene in the pot. The temperature ranges for the various fractions were: up to 47° C. for benzene and toluene, 47° to 61° C. for ethylbenzene, and 61° to 70° C. for styrene and part of the isopropylbenzene. The column made a sharp separation between styrene and α -methylstyrene as demonstrated by Figure 1. The yield of α -methylstyrene was calculated from the bromine numbers of the distillation charge and the distillate, assuming the presence of only two liquid olefins. The various hydrocarbons were identified by physical constants and solid derivatives. The amount of high boiling residue in the pyrolyzates and catalyzates was determined by topping a 25-gram sample under an absolute pressure of 1 mm., with the distilling tube at 45° C. and condensing tube at -78° C.

CATALYSTS

Three catalysts were tested: 99% alumina-1% nickel oxide made by impregnating activated alumina pellets (0.125-inch diameter) with nickel nitrate and decomposing the nitrate by heat; 85% alumina-15% chromia prepared by impregnating activated alumina pellets (0.125-inch diameter) with aqueous chromium

trioxide; and a four-component commercial dehydrogenation catalyst (4 to 8 mesh) which was essentially 72.4% magnesium oxide, 18.4% iron oxide, 4.6% potassium oxide, and 4.6% copper oxide (2). The first two catalysts were dried at 500 $^\circ$ to 600 $^\circ$ C. in a stream of air; the third catalyst was used without pretreatment. These catalysts were chosen because they had been shown to be effective in the dehydrogenation of certain other alkylated aromatic hydrocarbons. The exhausted catalysts were regeneratable by steam-air at 550° to 650° C. to their original activity.

RESULTS

Noncatalytic Dehydrogenation. At 0.7-second contact time (Table I) the optimal temperatures in the absence of steam for the once-through production of styrene and α -methylstyrene were 700° and 650° C., respectively; in the presence of steam the corresponding temperatures were 750° and 700° C. With regard to ultimate yields, the best production of styrene, both in the absence and presence of steam, was obtained at 700 ° C.; for α methylstyrene the optimal temperature was 650° C. in the absence of steam and 600 °C. in the presence of steam. Selectivity for α -methylstyrene production was decreased by adding steam and especially by raising the temperature. The best selectivity was at 600 $^{\circ}$ C., but the conversion at this temperature was not high enough to be commercially feasible. Demethanation increased as the temperature was elevated, and this increase was reflected by a falling off in the α -methylstyrene selectivity and by an increase in the paraffin content of the off-gas until in the vicinity of 700° C.; the extent of demethanation equaled that of dehydrogenation.

Catalytic Dehydrogenation. Catalytic dehydrogenation (Table II) was superior to noncatalytic dehydrogenation for the production of α -methylstyrene with respect to selectivity, conversion

TABLE I.	Noncatalyty	C DEHYDROG	ENATION OF	ISOPROPYL-
BENZENE D	N ABSENCE AN	VD PRESENCE	OF DILUEN	T STEAM AT
	0.7-Sec	ond Contact	T_{IME}	

	Withou	it Stea	m		With Steam					
600	650	700	750	600	650	700	750			
5.9	5,5	5.3	5.0	0.5	0.5	0.5	0.5			
$\begin{array}{c} 0 \\ 6 \end{array}$	$\begin{array}{c} 0 \\ 6 \end{array}$	$\begin{array}{c} 0 \\ 6 \end{array}$	$\begin{array}{c} 0\\ 3 \end{array} c$	$^{10}_{-6}$	$ \begin{array}{c} 10\\ 6 \end{array} $	$\begin{array}{c} 10 \\ 6 \end{array}$	$\begin{array}{c} 10 \\ 6 \end{array}$			
3.6 1.2 2.0 8.3 1.5 1.1 0.0	4.7 5.1 38.6 9.6 35.0 2.8 4.2 0.0	$10.0 \\ 5.7 \\ 16.0 \\ 21.9 \\ 24.3 \\ 11.7 \\ 10.3 \\ 0.1 \\$	$12.4 \\ 6.5 \\ 0.0 \\ 20.0 \\ 23.5 \\ 26.8 \\ 10.5 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.3 \\ 0.5 \\ 0.3 \\ 0.5 \\ 0.3 \\ 0.5 \\ 0.3 \\ 0.5 \\ 0.3 \\ 0.5 \\$	$ \begin{array}{c} 1.1\\ 0.4\\ 91.3\\ 1.4\\ 5.4\\ 0.2\\ 0.2\\ 0.0\\ \end{array} $	3.5 1.2 66.8 9.2 14.7 1.5 3.0 0.1	$\begin{array}{c} 7.4 \\ 4.2 \\ 20.6 \\ 24.4 \\ 24.9 \\ 8.8 \\ 9.5 \\ 0.2 \end{array}$	16.7 7.1 0.0 30.4 11.9 22.8 10.8 0.3			
	$\frac{16}{57}$	30 29 1.0	20 24 1.2	$ \begin{array}{r} 16 \\ 62 \\ 3.9 \end{array} $	$\frac{28}{44}$	31 31 1.0	30 12 0.4			
$72.3 \\ 4.7 \\ 9.1 \\ 13.9 \\ 1.1$	52.0 6.9 10.1 31.0 1.1	$31.3 \\ 9.8 \\ 6.3 \\ 52.6 \\ 1.0$	$34.2 \\ 13.7 \\ 5.1 \\ 47.0 \\ 1.0$	$64.0 \\ 4.0 \\ 5.6 \\ 26.4 \\ 1.0$	54.7 6.6 10.6 28.1 1.0	$39.6 \\ 12.3 \\ 7.1 \\ 41.0 \\ 1.0$	40.9 20.4 5.7 33.0 1.1			
	$\begin{array}{c} 600\\ 5.9\\ 0\\ 6\\ 82.2\\ 82.2\\ 1.1\\ 0.0\\ 11\\ 47\\ 72.3\\ 4.7\\ 9.1\\ 13.9\\ 1.1\\ \end{array}$	$\begin{array}{c cccc} & \text{Withou} \\ \hline & 000 & 650 \\ \hline & 5.9 & 5.5 \\ \hline & 0 & 0 \\ 6 & 6 \\ \hline & & & \\ 82.2 & 38.6 \\ 2.0 & 9.6 \\ 8.3 & 35.0 \\ 1.5 & 2.8 \\ 1.1 & 4.2 \\ 0.0 & 0.0 \\ \hline & & & \\ 111 & 16 \\ 47 & 57 \\ \hline & 4.3 & 3.6 \\ \hline & & \\ 72.3 & 52.0 \\ 4.7 & 6.9 \\ 9.1 & 10.1 \\ 13.9 & 31.0 \\ 1.1 & 1.1 \end{array}$	Without Stea 600 650 700 5.9 5.5 5.3 0 0 0 6.6 6 3.6 4.7 10.0 1.2 5.1 5.7 82.2 38.6 16.0 2.0 9.6 21.9 8.3 35.0 24.3 0.0 0.0 0.1 1.1 4.2 10.3 0.0 0.0 0.1 1.1 16 30 4.7 57 29 4.3 3.6 1.0 72.3 52.0 31.3 4.7 6.9 9.8 9.1 10.1 6.3 18.9 31.0 52.6 1.1 1.1 1.0	Without Steam 600 650 700 750 5.9 5.5 5.3 5.0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 6 6 6 3^c 3.6 4.7 10.0 12.4 1.2 5.1 5.7 6.5 82.2 38.6 16.0 0.0 2.0 9.6 21.9 20.0 8.3 35.0 24.3 23.5 1.5 2.8 11.7 26.8 1.1 4.2 10.3 10.5 0.0 0.0 0.1 0.3 111 16 30 20 4.7 6.9 9.8 13.7 9.1 10.1 6.3 5.1	Without Steam 600 650 700 750 600 5.9 5.5 5.3 5.0 0.5 0 0 0 0 0.5 0 0 0 0 10 6 6 6 3^c 6 82.2 38.6 16.0 0.9 91.3 2.0 9.6 21.9 20.0 1.4 8.3 35.0 24.3 23.5 5.4 1.5 2.8 11.7 26.8 0.2 1.1 4.2 10.3 10.5 0.2 0.0 0.0 0.1 0.3 0.0 11 16 30 20 16 47 5.7 29 24 62 4.3 3.6 1.0 1.2 3.9 72.3 52.0 31.3 34.2 64.0	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Without Steam With Steam 600 650 700 750 600 650 700 5.9 5.5 5.3 5.0 0.5 0.5 0.5 0.5 0 0 0 10 10 10 10 6 6 6 6 6 6 6 3.6 4.7 10.0 12.4 1.1 3.5 7.4 1.2 5.1 5.7 6.5 0.4 1.2 4.2 82.2 38.6 61.6 0.5 0.4 1.2 4.2 82.2 38.6 61.6 0.6 91.3 66.8 20.6 2.0 9.6 21.9 20.0 1.4 9.2 24.4 8.3 36.0 24.3 23.5 5.4 14.7 24.9 1.5 2.8 11.7 26.8 31.3 0.2			

^a Contact time at temperature of experiment calculated on the basis of total feed; free space taken as 60% of apparent volume. ^b Volume of liquid hydrocarbon per reactor volume per hour. ^c Exit end of reactor became plugged after 3 hours' operation. ^d Includes carbonaceous material deposited in reactor zone, plus carbon corresponding to CO and CO₂ in the off-gas; in the absence of steam there were only traces of cycles of carbon.

Credit was not taken for styrene which could be produced from by-product ethylbenzene.
 f Calculated on CO- and CO2-free basis.

March 1949

	Aluminum-Chromium Oxides					Aluminum-Nickel Oxides			Magnesium-Iron-Potassium-Copper Oxides								
O 1	Without steamWith steam					Withou	Without steam With steam		Without steam With steam								
Conditions Temperature, ° C. Liquid hourly space velocity b Water incomposition	600 5.9	$\begin{array}{c} 650 \\ 5.5 \end{array}$	$\substack{600\\0.5}$	$\substack{600\\0.5}$	650 0.9	$\substack{650\\0.5}$	$\begin{array}{c} 650 \\ 0.5 \end{array}$	600 5.9	$^{650}_{5.5}$	$\begin{smallmatrix} 600 \\ 0.5 \end{smallmatrix}$	$\begin{array}{c} 650 \\ 0.9 \end{array}$	$\begin{array}{c} 600 \\ 5,9 \end{array}$	$\substack{650\\5,5}$	600 0,5	$\begin{array}{c} 600 \\ 0,5 \end{array}$	$\begin{array}{c} 650 \\ 0.5 \end{array}$	$\substack{650\\0.5}$
mole ratio Hours	0 6	0 6	$\begin{array}{c} 10 \\ 6 \end{array}$	$\substack{10\\34}$		10 6	$\begin{array}{c} 10\\ 34 \end{array}$	0 6	0 6	$\begin{array}{c} 10\\ 34 \end{array}$		0 6	$\begin{array}{c} 0 \\ 6 \end{array}$	$10 \\ 6$	$\begin{array}{c} 10\\ 34 \end{array}$	$10 \\ 6$	$\begin{array}{c} 10\\ 34 \end{array}$
Weight yields, % of charge Benzene plus toluene Ethylbenzene Isopropylbenzene Styrene a-Methylstyrene Residue Gas Carbon ^c ,d	$ \begin{array}{r} 1.3\\ 1.5\\ 68.6\\ 0.8\\ 25.7\\ 0.4\\ 1.4\\ 0.3\end{array} $	$\begin{array}{r} 4.3 \\ 6.8 \\ 41.4 \\ 5.1 \\ 34.2 \\ 2.6 \\ 4.7 \\ 0.9 \end{array}$	0.8 0.8 83.4 1.1 13.0 0.2 0.6 0.1	$\begin{array}{c} 0.9 \\ 0.9 \\ 85.5 \\ 1.1 \\ 10.6 \\ 0.2 \\ 0.7 \\ 0.1 \end{array}$	$0.8 \\ 0.9 \\ 38.9 \\ 7.4 \\ 44.7 \\ 1.5 \\ 3.2 \\ 2.6$	2.8 3.4 15.4 11.2 57.6 1.6 6.0 2.0	2.3 3.4 29.2 9.2 48.0 1.3 4.6 2.0	$1.3 \\ 1.3 \\ 68.8 \\ 1.0 \\ 25.3 \\ 0.5 \\ 1.5 \\ 0.3 \\$	3.3 6.5 41.6 4.6 36.4 2.2 4.4 1.0	$\begin{array}{c} 0.5 \\ 0.4 \\ 91.5 \\ 0.1 \\ 6.9 \\ 0.1 \\ 0.4 \\ 0.1 \end{array}$	$\begin{array}{r} 4.6\\ 5.2\\ 24.1\\ 7.0\\ 48.7\\ 3.2\\ 4.1\\ 3.1 \end{array}$	$\begin{array}{c} 0.9 \\ 0.8 \\ 76.6 \\ 1.0 \\ 18.7 \\ 0.2 \\ 1.0 \\ 0.8 \end{array}$	3.9 4.4 50.4 7.4 26.0 2.4 4.7 0.8	$0.6 \\ 0.5 \\ 75.9 \\ 1.2 \\ 20.2 \\ 0.4 \\ 0.7 \\ 0.5 \\$	$0.8 \\ 0.7 \\ 76.7 \\ 1.0 \\ 18.5 \\ 0.3 \\ 1.1 \\ 0.9$	3.2 4.0 32.0 10.7 35.0 1.1 6.2 7.8	2.82.432.69.435.41.17.39.0
Ultimate yields, % of charge Styrene ^e α-Methylstyrene α-Methylstyrene/styrene, wt. ratio	3 82 27	9 58 6	7 78 11	8 73 9	12 73 6	13 68 5	13 68 5	3 81 27	8 62 8	1 81 80	9 64 7	4 80 20	15 53 4	84	4 80 20	16 52 3	14 53 4
Gas analysis, volume %1 Hydrogen Ethylene Propylene Paraffins Paraffin index	79.70.93.416.01.0	54.7 3.7 6.2 35.4 1.1	$83.1 \\ 2.0 \\ 0.6 \\ 14.3 \\ 1.0$	$74.9 \\ 3.1 \\ 0.4 \\ 21.6 \\ 1.1$	$86.0 \\ 1.5 \\ 0.3 \\ 12.2 \\ 1.1$	82.0 1.8 0.8 15.4 1.2	$76.4 \\ 4.5 \\ 0.8 \\ 18.3 \\ 1.1$	78.2 1.6 2.8 17.4 1.1	62.8 2.2 4.3 30.7 1.0	$69.7 \\ 1.5 \\ 4.0 \\ 24.8 \\ 1.0 \\ 1.$	$77.0 \\ 0.5 \\ 1.2 \\ 21.3 \\ 1.1$	$81.6 \\ 1.3 \\ 2.5 \\ 14.6 \\ 1.0$	$50.2 \\ 4.5 \\ 6.9 \\ 38.4 \\ 1.0$	$93.4 \\ 1.1 \\ 0.1 \\ 5.4 \\ 1.1$	$94.1 \\ 0.9 \\ 0.1 \\ 4.9 \\ 1.2$	$93.3 \\ 0.6 \\ 0.7 \\ 5.4 \\ 1.1$	$93.0 \\ 0.7 \\ 0.8 \\ 5.5 \\ 1.2$
^a Footnotes ^a , b, d, e, f are the se	ame as s	hown in	Table	I.													

TABLE II. CATALYTIC DEHYDROGENATION OF ISOPROPYLBENZENE IN ABSENCE AND PRESENCE OF DILUENT STEAM AT 0.7-SECOND CONTACT TIME^a

• In the presence of steam the regenerative ratio (carbon as oxides of carbon/carbon as carbonaceous deposit) was 0.2 to 2 for the Al $_2O_2$ -Cr $_2O_3$ and Al $_2O_2$ -NiO catalysts and 10 to 20 for the MgO-Fe $_2O_2$ -K $_2O$ -CuO catalyst.

per pass, and ultimate yield. In general, the extent of dehydrogenation was decreased at 600° C. and increased at 650° C. by the addition of steam. In both the absence and presence of steam the ultimate yield of styrene was increased and that of α -methylstyrene decreased by raising the temperature from 600° to 650° C. With the alumina-nickel oxide and the four-component oxide catalysts, steam had little or no effect on the ultimate yields. In the case of the alumina-chromia catalyst, the addition of steam at 650° C. benefited the ultimate yields of both styrene and α -methylstyrene.



genation Experiment

In the absence of steam the four-component oxide catalyst was the least selective of the three catalysts tested for the production of α -methylstyrene. However, in the presence of steam at 600° C., this catalyst gave the highest ultimate yield of α -methylstyrene at the commercially practical conversion per pass of 20%.

EXPLORATORY TEST RUN

A 216-hour run (Figure 2) was made in a copper-lined reactor as an exploratory test of the life of the four-component oxide catalyst for the production of α -methylstyrene. The operating conditions were as follows: The molal ratio of steam to hydrocarbon, the volume of isopropylbenzene per volume of catalyst per hour, the temperature, and the contact time were, respectively, 20 to 1, 0.2, 625° C., and 0.7 second. Throughout the 216 hours the catalyst showed no depreciation in activity or selectivity; in fact, activity and selectivity increased slowly with time. The average α -methylstyrene conversion per pass was 43%, the ultimate yields of α -methylstyrene and styrene were 71 and 10%, respectively, and the hydrogen content of the exit gas was 96 mole %.

CONCLUSION

The catalytic dehydrogenation of isopropylbenzene can be made to give acceptable yields of α -methylstyrene. For example, the four-component oxide catalyst at 600° C. in the presence of steam gave an 84% ultimate yield of α -methylstyrene at the conversion of 20% per pass. To this can be added a 5% ultimate yield of styrene, making a total of 89% which is to be compared with the catalytic dehydrogenation of ethylbenzene under the same conditions whereby an 88% ultimate yield of styrene was obtained. Isopropylbenzene is not a preferable stock for the commercial production of styrene, noncatalytically or catalytically.

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