Patented Feb. 19, 1946 2,395,161

UNITED STATES PATENT OFFICE

2,395,161

PRODUCTION OF XYLENE AND TOLUENE AND OTHER LIGHT COAL TAR OILS

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No Drawing. Application February 16, 1944, Serial No. 522,670. In Great Britain April 8, 1942

3 Claims. (Cl. 260—672)

The present invention relates to the production of xylene and toluene and other light coal-tar oils.

It is known that toluene can be produced by demethylation of xylene. We have now found that liquid products from the destructive distillation of coal which boil above 155° C. can be cracked at elevated temperatures to produce substantial yields of xylene and toluene, or of other light oils rich in benzene and toluene.

Heavy naphtha is an example of these products which we have found to be particularly suitable. It represents the heavy ends from either crude benzole stripped from coal-gas or the light oils distilled from tar. The main constituents are the trimethylbenzenes (chiefly pseudocumene and mesitylene) together with smaller amounts of tetramethylbenzene. In an unwashed naphtha, indene and coumarone are also present, while in washed naphtha these have been removed; either washed or unwashed naphtha can be used according to this invention. The operation of the invention is in no way prejudiced by the use of stocks containing paraffin or petroleum oils, since such constituents are broken down in the process, enhancing the calorific enrichment of the carrier gas which is a feature of the invention.

The process is preferably carried out with the addition of hydrogen or a gas containing hydrogen, such as coal gas, and advantageously at temperatures of 650–900° C., for example at 800° C. or 850° C.

After refinement by the ordinary processes of rectification and washing, toluene produced by this process had a specific gravity of 0.871, corresponding to a purity of more than 99%.

By raising the temperature of operation, the ratio of the constituents in the liquid product is displaced in favour of the lower members of the benzene series. To obtain a light oil rich in benzene and toluene, without considerable increase of gas and pitch formation, the process may advantageously be carried out at 850° C.

Methods of carrying the invention into effect will now be described by way of examples.

Example I.—Dorman Long & Co.'s Heavy Naphtha, boiling range 5/95 ml. 163–175° C., was used as cracking stock; fractionation through a vacuum-jacketed Podbielniak type column indicated approximately 75% trimethylbenzenes. 1000 ml. of this naphtha, entrained in a stream of coal gas, was gradually introduced into an iron tube of 1'' diameter, packed with coke and heated to 750°. The ratio of coal-gas to naphtha vapour was 8:1, and the time of contact 0.25 sec. The products of cracking were condensed through a series of condensers, and the issuing gas scrubbed through two wash oil scrubbers. The wash oil was blown with stream, and the recovered aromatics added to the main liquid bulk from the condensers. The composition of this product in terms of benzene, toluene, xylene, trimethylbenzene and polymerized material (boiling above 175° C.) was determined by fractionation through the Podbielniak column. The portion boiling between 125° and 175° C. (xylene and trimethylbenzene) was re-cycled, and the corresponding portion from the re-cycle products was put through the operation yet a third time.

The collected results are given below, all figures being percentages of the original charge of heavy naphtha.

	Charge	Liquid yield	Benzene	Toluene	Xylene	Trimethylbenzene	Polymerized material	Gas (difference)
1st pass	100	74.1	2.1	6.5	17.2	27.9	20.4	25.9
2nd pass	17.2+27.9=45.1	41.5	0.7	4.3	16.4	12.9	7.1	3.6
3rd pass	16.4+12.9=29.3	27.2	0.3	2.6	12.8	6.9	4.6	2.1
Total product			3.1	13.1	12.8	6.9	32.1	31.6

The composition of the gas entering and leaving the cracking unit was as follows: Entering—47.9% hydrogen, 24.9% saturated hydrocarbons, 2.9% unsaturated hydrocarbons, 0.5% oxygen, 2.7% carbon dioxide, 12.0% carbon monoxide, 9.1% nitrogen: Leaving—respectively, 42.9%, 29.4%, 5.7%, 0.0%, 2.4%, 11.6%, 8.0%.

These analyses show that the output gas has a good calorific value and is quite suitable for passing to a main gasholder.

Example II.—100 ml. of heavy naphtha as used in Example I was entrained in coal gas and cracked by passage through an empty iron tube heated to 850° C. The ratio of coal-gas to naphtha vapour was 10:1, and the contact time 0.5 sec. In other respects the procedure was as in the first pass in Example I, except that the wash-oil was replaced by an active carbon scrubber. The products, as percentages of the charging stock,

were as follows: Total liquid yield, 67.8; benzene, 7.0; toluene, 13.6; xylene, 14.1; trimethylbenzene, 16.3; polymerized material, 16.8; gas (difference), 32.2.

Example III.—Heavy naphtha, at the rate of 1 gallon per hour, and debenzolized coal-gas of calorific value 530 B. t. u. per cu. ft. (containing 55% hydrogen, 0.3% oxygen, 6.8% nitrogen, 1.8% carbon dioxide, 6.4% carbon monoxide, 26.7% saturated hydrocarbons and 3.0% unsaturated hydrocarbons) at the rate of 300 cu. ft. per hour, were pumped to a pre-heater at 650° C., and thence passed to the reaction chamber at 800° C. Each of these vessels consisted of an iron pipe 5 feet long and 6 inches in diameter, packed with broken brick and directly fired. The ratio of coal-gas to naphtha in the vapour phase was 10 volumes to 1, and the time of contact at 800° C. was 0.56 second.

From the reaction chamber, the products passed through a water-cooled condenser to a separator where the bulk of the liquid products was collected. The gas stream thence passed upwards through a tower against a downward spray of water, to remove tar fog. The defogged gas flowed to an active carbon unit for the removal of the small proportion of condensible hydrocarbon vapours which was not removed by the first condenser; these hydrocarbons were recovered by steaming.

The combined liquid oil products were distilled, to remove benzene, toluene and polymerized products, and the intermediate fractions subjected again to the cracking cycle. This process was twice repeated, making a total of four cycles in all.

The overall yields (per cent. by weight of the original naphtha) for the whole experiment were:

Oil B. P. to 95° C. (benzene)	5.3
Oil B. P. 95–125° C. (toluene)	19.9
Oil B. P. 125–175° C. (xylenes and trimethylbenzenes)	11.4
Residue distilling above 175° (polymerized material)	31.3
Gas, pitch and loss	32.1
	100.0

The yields of toluene in the four cycles were respectively 12.1, 4.8, 1.8 and 1.2 per cent. On continuous cycling in which the whole of the 125–175° fraction (mixed with fresh naphtha) was ultimately cracked, the yield of toluene would, according to the findings quoted, be 22 to 23 per cent. of the weight of naphtha from which it is derived, and the only other products would then be benzene, polymerized material and gas.

The rate of flow of the uncondensible gases finally leaving the apparatus was not less than the flow supplied as carrier. Owing to the formation of gaseous hydrocarbons, the output gas was markedly higher in calorific value than the input. Analysis after the first cycle showed 49.3% hydrogen, 33.3% saturated hydrocarbons, 5.9% unsaturated hydrocarbons, 0.1% carbon dioxide, 5.9% carbon monoxide and 5.5% nitrogen, the calorific value being 640. In the second and subsequent cycles this effect was naturally much less marked. In continuous re-cycling of the xylene fraction with fresh naphtha, the overall increase of calorific value, calculated from the observed data, would be about 50 B. t. u. per cu. ft.

We claim:

1. A process for demethylating methylated benzene hydrocarbon charging stocks containing nine and ten carbon atoms and simultaneously producing a gas of enhanced calorific value which comprises in combination the following steps: entraining vapours containing said hydrocarbons in a current of coal gas, subjecting said current to pyrolysis with a contact time ranging from 0.25 to 0.56 second and at a temperature between 650 and 900° C., fractionating the products, stripping off C_6–C_8 hydrocarbons and recycling the intermediate fraction boiling at from 125–175° C. for pyrolytic treatment.

2. A process for demethylating methylated benzene hydrocarbon charging stocks containing nine and ten carbon atoms and simultaneously producing a gas of enhanced calorific value which comprises in combination the following steps: entraining vapours containing said hydrocarbons in a current of coal gas, the ratio of hydrocarbon to coal gas being 1 to 8, subjecting said current to pyrolysis with a contact time of 0.26 sec. and at a temperature between 650 and 900° C., fractionating the products, stripping off C_6–C_8 hydrocarbons and recycling the intermediate fraction boiling at from 125–175° C. for pyrolytic treatment.

3. A process for demethylating methylated benzene hydrocarbon charging stocks containing nine and ten carbon atoms and simultaneously producing a gas of enhanced calorific value which comprises in combination the following steps: entraining vapours containing said hydrocarbons in a current of coal gas, the ratio of hydrocarbon to coal gas being 1 to 10, subjecting said current to pyrolysis with a contact time of 0.5–0.56 sec. and at a temperature between 650 and 900° C., fractionating the products, stripping off C_6–C_8 hydrocarbons and recycling the intermediate fraction boiling at from 125–175° for pyrolytic treatment.

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