Oct. 5, 1965 D. K. CHAPMAN 3,210,434

PRODUCTION OF PHENYLNAPTHALENE

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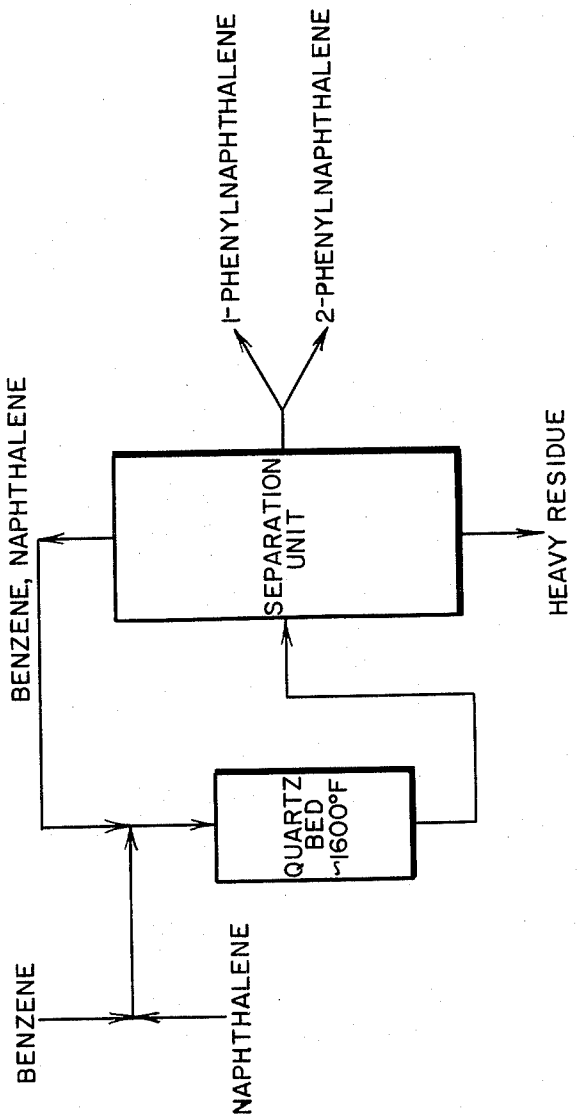

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PRODUCTION OF PHENYLNAPTHALENE

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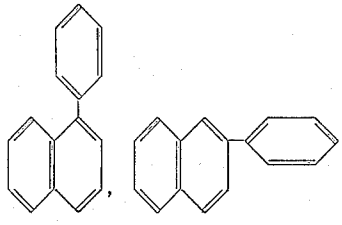
9 Claims. (Cl. 260—670)

This invention relates to the production of phenylnaphthalene directly from benzene and naphthalene.

Phenylnaphthalene has the empirical formula

$$C_6H_5C_{10}H_7$$

It exists in two isomeric forms, which are conventionally designated as 1-phenylnaphthalene and 2-phenylnaphthalene:

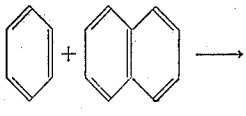


1-phenylnaphthalene has a melting point of 113° F, and boils at 617° F. 2-phenylnaphthalene melts at 216.5° F. and boils at 657° F. The phenylnaphthalenes can be used as heat exchange media and chemical intermediates, as well as for other purposes.

A primary objective of this invention has been to provide an economical process for producing phenylnaphthalene in substantial yields, from commercially available starting materials.

I have empirically discovered a process whereby both 1- and 2-phenylnaphthalene may readily be synthesized from benzene and naphthalene. In accordance with this process, a mixture of naphthalene and benzene, in a certain range of mol ratios, is contacted with an inert bed, for example, packed with quartz or ceramic chips, at a temperature in excess of substantially 1400° and preferably at about 1600° F.

At these conditions the benzene and naphthalene apparently undergo thermal pyrolysis. The over-all reaction may be illustrated:



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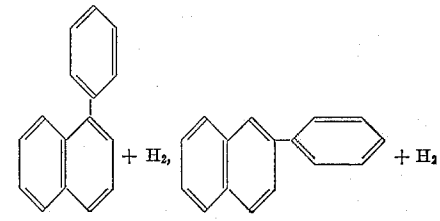

As will be shown, the relative yields of 1-phenylnaphthalene and 2-phenylnaphthalene are in the ratio of approximately 1:2, as theory would suggest.

The mol ratio of benzene to naphthalene in the input stream is important for obtaining the best yield. This ratio should preferably be above 2:3; with larger proportions of naphthalene, coking is severe. The best conversion results are obtained when the benzene/naphthalene ratio is about 3:2.

Residence time, as measured by superficial velocity in the reaction zone, also beats an important relation to yield and to the degree to which high boiling residues and coke are formed. I believe that the residence time should preferably be in the range of about 0.5 to 2 seconds; about 1.4 seconds is optimal at 1600° F. In general, coking and formation of high boiling compounds tend to increase with longer residue times.

An important feature of the process I have discovered is that it may be carried out at atmospheric pressures, thereby making possible the use of inexpensive equipment. Moreover, the reaction will proceed in the absence of added hydrogen, thus eliminating the need for a separate source of hydrogen.

The accompanying drawing is a flow sheet illustrating the preferred practice of this process.

In accordance with a preferred example of the process I have discovered, a feed comprising approximately 59 mol percent benzene and 41 mol percent naphthalene, both technical grade, was passed down flow through a bed of an inert material such as quartz chips or ceramic beads. The bed was externally heated, and peak temperature was 1594° F. Residence time in the bed at temperatures over 1500° F. was 1.42 seconds. The process was conducted in the absence of added hydrogen and at atmospheric pressure. The liquid product yield was 94.3% of the feed, and the liquid product comprised 3.7% 1-phenylnaphthalene, 7.1% 2-phenylnaphthalene, 20.2% benzene, and 55.4% naphthalene. 7.1% biphenyl was formed as a side product, together with 6.5% of coke and compounds having boiling points higher than 2-phenylnaphthalene. The increased proportion of naphthalene was apparently due to synthesis from benzene. If biphenyl is converted to benzene, which can be done by known technology, and the converted benzene is recycled together with unreacted benzene and naphthalene from the primary reaction, ultimate theoretical yields of 20.2% 1-phenylnaphthalene and 38.7% 2-phenylnaphthalene could be expected.

The following table illustrates practice of this process over a range of residence times, temperatures, and feed ratios.

TABLE

Operating conditions and product analysis

Run Number	BPN-6B	BPN-6C	BPN-6D	BPN-7	BPN-8	BPN-11	BPN-13	BPN-14
Residence Time, over 1,500° F., Sec	1.02	1.20	1.42	1.63	1.83	1.23	1.44	0.0
Peak Temperature, ° F	1,590	1,591	1,594	1,590	1,590	1,569	1,555	1,404
Feed:								
Benzene, Mol percent	59	59	59	53	64	81	40	61
Naphthalene Mol percent	41	41	41	47	36	19	60	39
Product Yield, Wt. percent	87.7	93.0	94.3	85.0	90.1	92.0	85.4	91.0
Product Analysis, Wt. percent:								
Benzene	22.9	31.8	20.2	33.1	43.8	58.6	20.9	40.6
Naphthalene	58.8	48.7	55.4	48.7	41.8	23.2	58.2	56.3
Biphenyl	5.1	4.9	7.1	3.4	5.6	10.5	5.4	1.8
1-Phenylnaphthalene	3.2	3.3	3.7	2.8	2.3	1.8	2.3	0.5
2-Phenylnaphthalene	5.6	6.4	7.1	5.9	4.6	3.6	4.5	0.8
>2-Phenylnaphthalene	4.4	4.9	6.5	6.1	1.9	2.3	8.7	0.0
Yield of 1- and 2-Phenylnaphthalene and Higher Boiling compounds:								
1-Phenylnaphthalene	21.3	21.1	20.2	16.1	23.6	21.5	12.7	35.0
2-Phenylnaphthalene	37.2	40.8	38.7	33.9	47.1	43.1	24.8	56.0
>2-Phenylnaphthalene	29.3	31.2	35.4	35.1	19.5	27.5	47.9	0.0

From the table it will be apparent that the yields of 1- and 2-phenylnaphthalene are poorest at an operating temperature of about 1400° F. (Run BPN–14), and that in general much better yields are obtained at temperatures of about 1600° F. As illustrated by Run BPN–6D, which corresponds to the specific example previously given, the best conversions at 1600° F. are obtained at residence times of about 1.4 seconds and at a feed ratio of approximately 3 mol parts benzene to 2 mol parts naphthalene. At times these operating conditions, residence times in excess of about 1.4 seconds tend to cause progressively poorer yields of 1- and 2-phenylnaphthalene, although the yields are nonetheless better than the yield obtained at about 1400° F.

The reaction is a thermal reaction, and does not require a catalyst. Reactor design is not believed to be critical; while a downflow bed of quartz chips or beads is preferred, the reactor might also comprise any configuration in which the reactants are passed through or over an inert material heated directly or indirectly.

Following passage through the reactor, the resultant mixture, which typically will comprise benzene, naphthalene, biphenyl produced as a side reaction product, and 1- and 2-phenylnaphthalenes, together with higher boiling compounds, is passed through a conventional fractionation or separation zone. The separation of the desired phenylnaphthalenes from this mixture may be accomplished, by way of example, by fractionating a cut comprising a relatively pure mixture of 1- and 2-phenylnaphthalenes. This cut is then separated into its phenylnaphthalene components by fractional crystallization.

The very low conversions at temperatures of about 1400° F. indicate that the operating temperature should preferably be above that temperature. The mol ratio of benzene to naphthalene should be higher than about 2:3, because of the poor conversion at that ratio, as exemplified by Run BPN–13, in which there was a large conversion to high boiling materials that ultimately resulted in plugging the reactor.

Having described my invention, what is claimed is:

1. The method of producing phenylnaphthalene comprising,
   passing a mixture of benzene and naphthalene in contact with an inert bed at a temperature in the range of substantially 1400°–1600° F.,
   said mixture comprising at least 2 mol parts benzene and 3 parts naphthalene,
   the mixture being maintained in contact with the bed for a residence time of between about 0.5 and 2 seconds,
   and separating phenylnaphthalene from the mixture so treated.

2. The method of producing phenylnaphthalene comprising,
   passing a mixture of benzene and naphthalene in contact with an inert bed at a temperature of at least 1400° F.,
   said mixture comprising at least 2 mol parts benzene to 3 parts naphthalene,
   the mixture being maintained in contact with the bed for a residence time of between about 0.5 and 2 seconds,
   and separating phenylnaphthalene from the mixture so treated.

3. The method of claim 2 wherein the benzene/naphthalene mol ratio of said mixture is in the range of about 2/3 to 4/1.

4. The method of producing phenylnaphthalene comprising,
   passing a mixture of benzene and naphthalene in contact with an inert bed at a temperature of about 1600° F.,
   said mixture comprising about 3 mol parts benzene to about 2 parts naphthalene,
   the mixture being maintained in contact with the bed for a residence time of between about 1.0 and 1.8 seconds,
   and separating 1- and 2-phenylnaphthalene from the mixture so treated.

5. The method of producing phenylnaphthalene comprising,
   passing a mixture of benzene and naphthalene in contact with an inert bed of quartz bodies at a temperature of about 1600° F.,
   said mixture comprising about 3 mol parts benzene to about 2 parts naphthalene,
   the mixture being maintained in contact with the bed for a residence time of between about 1.0 and 1.8 seconds,
   and separating 1- and 2-phenylnaphthalene from the mixture so treated.

6. The method of producing 1- and 2-phenylnaphthalene comprising,
   passing a mixture of benzene and naphthalene in contact with a quartz bed at a temperature of about 1500°–1600° F. and at substantially atmospheric pressure,
   the benzene/naphthalene mol ratio of said mixture being about 3/2,
   the mixture being maintained in contact with the bed for a residence time of about 1.0–1.8 seconds,
   and separating 1- and 2-phenylnaphthalene from the mixture so treated.

7. The method of claim 6 wherein said residence time is about 1.4 seconds and wherein said temperature is about 1600° F.

8. The method comprising,

subjecting a mixture of benzene and naphthalene to pyrolysis at a temperature of at least 1400° F.,

said mixture comprising at least 2 mol parts benzene to 3 parts naphthalene,

the mixture being maintained at said temperature for a period of between about 0.5 and 2 seconds,

and separating phenylnaphthalene from the mixture so treated.

9. The method of producing phenylnaphthalene comprising, passing a mixture of benzene and naphthalene in contact with an inert bed at a temperature in the range of substantially 1400°–1600° F., said mixture comprising at least 2 mol parts benzene to 3 mol parts naphthalene, the mixture being maintained in contact with the bed for a residence time of between about 0.5 and 2 seconds, separating phenylnaphthalene, by-product diphenyl, and unreacted benzene and naphthalene from the effluent, converting the diphenyl to benzene and recycling benzene from the next previous step together with the separated unreacted benzene and naphthalene to the reaction zone.

References Cited by the Examiner

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,210,434 October 5, 1965

Duane K. Chapman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 20, for "beats" read -- bears --; line 26, for "residue" read -- residence --; column 3, line 33, strike out "times"; line 70, for "and" read -- to --.

Signed and sealed this 3rd day of May 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents