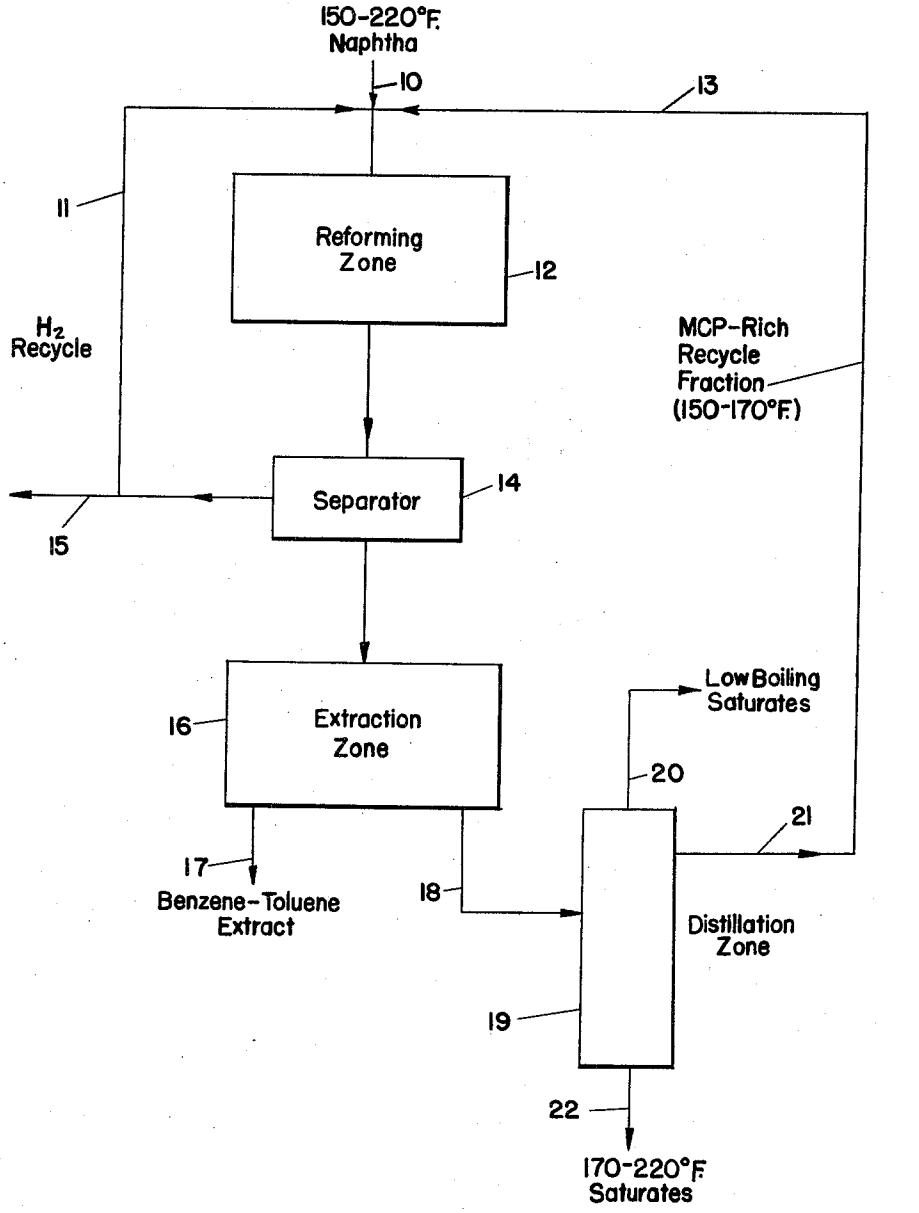
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PREPARATION OF BENZENE AND TOLUENE

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PREPARATION OF BENZENE AND TOLUENE

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This invention relates to the preparation of benzene and toluene by reforming low boiling naphtha containing C_6 and C_7 naphthenes and more particularly is directed to a method for increasing the quantity of benzene produced by reforming a naphtha boiling in the range of 150–220° F. in the presence of a platinum-containing reforming catalyst.

Commercial processes for the production of aromatics such as benzene and toluene by dehydrogenation of the naphthenes present in the low-boiling fractions of straight-run petroleum naphthas with concomitant isomerization and hydrocracking of the acyclic components of the feed to a higher octane gasoline fraction, are well known to the art. In such processes the feed stock is contacted with a catalyst in the presence of added hydrogen, at temperatures of from about 875° F. to 975° F. and at a pressure of from about 200 p.s.i.g. to about 600 p.s.i.g. A preferred catalyst for this type of operation comprises platinum impregnated on an alumina base, and the catalyst advantageously may contain a minor amount (e.g., 0.1 to 6.0%) of combined halogen. Generally the platinum content of the catalyst is in the range of 0.1% to about 1.0%. Such catalysts possess dehydrogenation, isomerization and hydrocracking activities, and these activities are so balanced in the manufacture of the catalyst as to insure a maximum of dehydrogenation and isomerization activity but not sufficient hydrocracking activity to crack such straight chain paraffins as are not isomerized to isoparaffins during the reaction. The aromatics produced in the hydroforming operation conventionally are extracted from the reformate by means of a suitable solvent such as diethylene glycol containing a minor amount of water.

Reactions involved in the production of benzene involve dehydrogenation of cyclohexane and isomerization of methylcyclopentane to cyclohexane followed by dehydrogenation. In the production of toluene the reactions are dehydrogenation of methylcyclohexane, isomerization of dimethylcyclopentane to methylcyclohexane followed by dehydrogenation, and dehydrogenation and dehydrocyclization of heptane. In commercial practice the conversion of cyclohexanes to aromatics by means of the platinum-containing reforming catalyst occurs nearly completely or in other words, the yield of aromatics from the cyclohexane components of the naphtha charge approaches 100%. Also the conversion of dimethylcyclopentane to toluene is high. However, the conversion of methylcyclopentane to benzene characteristically is relatively low. Hence, the yield of benzene in conventional commercial practice generally is substantially lower than otherwise would be obtained if all the methylcyclopentane were converted.

An object of the present invention is to obtain a substantial increase in the benzene yield resulting from reforming a low boiling straight run naphtha.

In one embodiment of the invention, a straight run naphtha boiling in the range of 150–220° F. is subjected to hydroforming conditions, including a temperature in the range of 875–975° F. and a pressure in the range of 200–600 p.s.i.g., in the presence of a platinum-containing reforming catalyst. The resulting reformate is extracted to separate a benzene-toluene extract from a saturated hydrocarbon raffinate which contains unconverted methylcyclopentane. The raffinate is then distilled to separate

a fraction enriched in methylcyclopentane. This methylcyclopentane-rich fraction is recycled to the reforming step by hydroforming in admixture with the virgin charge. In this manner conversion of the methylcyclopentane to benzene is maximized and a substantial increase in the benzene yield is achieved.

The invention can also be practiced in a modified manner by hydroforming the methylcyclopentane-rich fraction, obtained in the manner above described, in a separate reforming operation instead of in admixture with the virgin naphtha charge. In commercial practice this can be done conveniently by utilizing a blocked-out type of operation and alternately charging the virgin naphtha and the methylcyclopentane-rich fraction to the reformer. The reformate obtained from hydroforming the methylcyclopentane-rich fraction can be extracted either separately or in admixture with raffinate obtained from the hydroformed virgin naphtha to remove the benzene and the resulting raffinate can be distilled, either alone or in admixture with raffinate obtained from processing the virgin naphtha, to separate a fraction rich in unconverted methylcyclopentane which can be reprocessed.

The invention is more specifically described in conjunction with the accompanying drawing which is a schematic flowsheet illustrating one manner of practicing the invention. The charge to the process is a straight run naphtha fraction boiling in the range of 150–220° F., which typically may have the following composition:

	Percent
Methylcyclopentane	6
Cyclohexane	7
Methylcyclohexane	12
Dimethylcyclopentane	11
Benzene	2
Toluene	4
Paraffins	58
	100

Referring to the drawing, the charge naphtha, which enters the system through line **10**, is admixed with recycle hydrogen from line **11** and the mixture is heated by means not shown to a suitable reforming temperature in the range of 875–975° F., more preferably 910–960° F., and introduced to reformer **12**. A recycle fraction obtained as hereinafter described is also fed to the reformer via line **13**. The reformer contains a platinum type reforming catalyst which preferably contains a minor amount of combined halogen. Reforming zone **12** may comprise a series of reactors with heaters between the reactors for supplying heat absorbed due to the endothermic reactions involved, as is customary in conventional reforming operations. The reforming zone should be operated at a pressure in the range of 200–600 p.s.i.g., the molar ratio of hydrogen to hydrocarbon fed thereto should be in the range 2:1 to 5:1 and the space rate in the reactors should be in the range of 1–5 volumes of hydrocarbon per volume of catalyst per hour. The products from the reforming step pass to condensing and separating means, indicated at **14**, from which hydrogen is recycled through line **11** with excess hydrogen being withdrawn from the system via line **15**.

The liquid reformate from separator **14** passes to extraction zone **16** for separation of the aromatics from nonaromatic hydrocarbons. Zone **16** preferably is a solvent extraction zone in which countercurrent contact of the reformate with a selective solvent, such as diethylene glycol containing a minor amount of water, is effected to dissolve the aromatics and the extracted aromatics are thereafter stripped from the solvent. Alternatively, extraction zone **16** can employ a selective adsorbent such as silica gel instead of a solvent. The resulting extract,

which is removed through line **17**, is a mixture of benzene and toluene which thereafter can be distilled to isolate the individual aromatics.

Raffinate which leaves the extraction zone via line **18** typically may amount to about 60% by volume of the virgin naphtha charged and have the following composition:

	Percent
Methylcyclopentane	6.8
Cyclohexane	0.3
Methylcyclohexane	0.1
Dimethylcyclopentanes	2.2
Benzene	0.1
Toluene	2.5
Paraffins	88.0
	100.0

Comparison of this composition with that given hereinbefore for the charge shows that conversion of the cyclohexanes and dimethylcyclopentanes during the reforming step is high but that the conversion of methylcyclopentane is relatively low.

The raffinate from line **18** passes to distillation zone **19** which is operated in a manner to segregate a heart cut which is rich in methylcyclopentane, preferably containing at least 15% of this component. A light saturate fraction which boils (say) below 150° F. is removed through overhead line **20**, the methylcyclopentane-rich fraction, which, for example, may boil through the range of 150–170° F., is taken as a sidestream through line **21**, and a heavier saturate fraction boiling in the range of 170–220° F. is obtained as bottoms via line **22**. Typical yields of these fractions based on the raffinate charged to distillation zone **19** are 30% of the low boiling saturates, 20% sidestream fraction containing about 25% methylcyclopentane, and 50% bottoms fraction. The methylcyclopentane-rich fraction is recycled through line **13** for reforming in admixture with the virgin naphtha.

As previously stated the methylcyclopentane-rich fraction alternatively can be subjected separately to hydroforming conditions in either another reforming zone or in zone **12** utilizing a blocked-out operation. When this is done, milder hydroforming conditions generally should be used, as compared to the conditions for hydroforming the virgin naphtha, due to the greater tendency of methylcyclopentane to crack during reforming as compared to the other naphthenes in the virgin naphtha.

I claim:

1. Method of preparing benzene and toluene which comprises reforming a mixture of straight run naphtha boiling in the range of 150–220° F. with hereinafter specified recycle fraction in the presence of a platinum-containing reforming catalyst, said reforming being carried out in the presence of hydrogen at a pressure of 200–600 p.s.i.g., a molar ratio of hydrogen to hydrocarbon in the range of 2:1 to 5:1 and a temperature of 875–975° F., separating gaseous components from the reformate, directly extracting the reformate to separate a benzene-toluene extract from saturated hydrocarbon raffinate containing unconverted methylcyclopentane, distilling the raffinate to separate a methylcyclopentane-rich fraction boiling in the range of 150–170° F. from lower and higher boiling hydrocarbons, and recycling all said methylcyclopentane-rich fraction as the said recycle fraction.

2. Method of preparing benzene and toluene which comprises reforming a straight run naphtha boiling in the range of 150–220° F. in the presence of a platinum-containing reforming catalyst, said reforming being carried out in the presence of hydrogen at a pressure of 200–600 p.s.i.g., a molar ratio of hydrogen to hydrocarbon in the range of 2:1 to 5:1 and a temperature of 875–975° F., separating gaseous components from the reformate, directly extracting the reformate to separate a benzene-toluene extract from saturated hydrocarbon raffinate containing unconverted methylcyclopentane, distilling the raffinate to separate a methylcyclopentane-rich fraction boiling in the range of 150–170° F. from lower and higher boiling hydrocarbons, and reforming all said methylcyclopentane-rich fraction in the presence of a platinum-containing catalyst under the above-specified reforming conditions to convert methylcyclopentane to benzene.

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