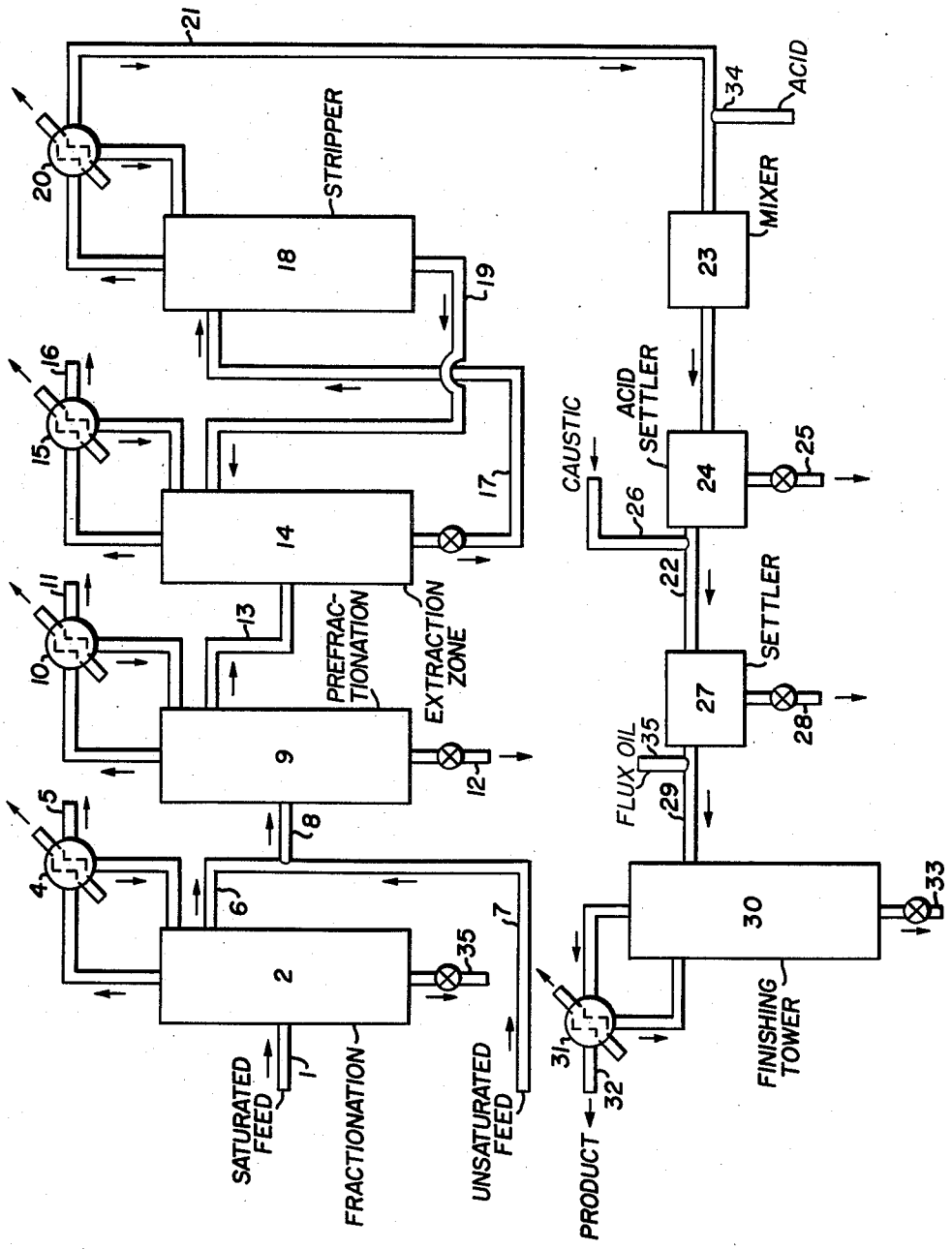
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BENZENE RECOVERY FROM MIXED STEAM CRACKED HYDROFORMATE FEED UTILIZING PREFRACTIONATION

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BENZENE RECOVERY FROM MIXED STEAM CRACKED HYDROFORMATE FEED UTILIZING PREFRACTIONATION

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This invention deals with the purification of C_6–C_7 aromatic hydrocarbons and especially benzene from mixed crue feed stocks, one of which is essentially a saturated or hydrogenated stock, e.g., hydroformate, the other being a stock containing unsaturates, e.g., thermally cracked naphtha.

The present process relates to an improved method of benzene recovery which comprises mixing a crude unsaturated stock having a wide boiling range, e.g., C_5 cut up to 160° C. with a more narrow boiling range benzene cut, e.g., 60° to 96° C. from a saturated stock such as a hydroformate fraction, and fractionating the mixture prior to extractive distillation.

It has been suggested in U.S. Patent 2,718,492 to R. T. Leary and F. W. Banes that a feed stock containing unsaturated hydrocarbons having substantially higher boiling points than benzene, be added in proper proportions to an essentially saturated feed stock to obtain a mixed feed stock more suitable to the extractive distillation step, and recovery of high grade benzene.

In the extractive distillation of this prior art procedure, a certain amount of the olefinic components were made to remain preferentially with the benzene in the solvent extract thereby displacing saturated hydrocarbon impurities. The extracted olefinic impurities were essentially and completely removed from the benzene after it was stripped from the solvent by treatment with concentrated sulfuric acid followed by settling to remove acid sludge, neutralization and redistillation. In the acid stripping step, there will be some benzene loss which is dependent primarily upon the amount of olefinic and diolefinic impurities in the solvent extract. The amount of benzene loss in the acid treating steps will be proportional to the amount of said impurities.

In the present process, benzene is first recovered as a side stream concentrate from the hydroformer fractionating towers at extremely high recovery due to the relatively wide boiling range cut taken. Saturated high boiling components which may have been present in this hydroformate, e.g., those boiling between about 85° to 96° C. will be rejected with no benzene loss when the mixed stocks undergo prefractionation in accordance with the invention. Introduction of paraffins into the mixed feed fractionator permits removal of about twice as much of difficultly removable olefins and diolefins, e.g., cyclohexene and cyclohexadiene, as would be possible if steam cracked feed alone were treated. The present process also results in the decrease in phenol losses due to removal of peroxides and moisture from the hydroformate feed during the mixed feed distillation. The amount of phenol loss due to sludge formation is decreased since in the present process, the hydroformate component will be freshly distilled, i.e., quickly transferred to the extractive distillation zone without substantial delay.

In the aforementioned process of U.S. Pat. 2,718,492, it was proposed that the saturated feed stock be cut so that the end point was no more than about 5° C. above the boiling point of benzene, i.e., a maximum end point of

85° C. This step was regarded as necessary in order to obtain benzene of high purity. The unsaturated feed stock contained C_6 and C_7 olefins having boiling points up to about 95° C.

It has now been discovered that if certain prefractionating steps are taken prior to the extractive distillation of mixed saturated and unsaturated feed stocks, recovery of benzene in greater improved yields and purity may be obtained. More specifically, a 60°–85° C. cut taken as a side stream from the mixed feed prefractionator will contain about 95% of the benzene based on the combined feed. The following tables illustrate the boiling point distribution for a light hydroformate and a vapor phased cracked naphtha distillate:

TABLE I

Analytical distillation of hydroformate

[30 plates 15/1 reflux ratio.]

Temp., °C.	Vol. Percent OH	Benzene Content of Cut, percent	Percent of Total Benzene in Cut
59.4	7.0	0.11	0.1
65.5	9.0	4.0	4.1
71	11.0	12.96	13.2
73.9	13.0	30.78	31.2
82.8	15.0	24.72	24.9
86.7	17.0	10.07	10.0
90.6	19.0	7.00	7.4
93.9	20.9	4.28	4.6
94.6	22.9	2.67	2.8
97.2	24.8	1.56	1.7
			100.0

TABLE II

Analytical distillation of vapor phased cracked naphtha distillate [1]

[30 plates 15/1 reflux ratio]

Temp., ° C.	Vol. Percent OH	Benzene Content, Vol. Percent of Cut
33.5	0	
60	30	
63	34	
64.5	36	
65.5	40	8
66.7	44	10
72.8	46	18
75.6	48	30
77.2	50	48
78	52	60
80	68	80
91	70	54
95	72	10
107	76	1
131	98	
143.3	[2]	

[1] Composition comprises benzene, olefins and diolefins with little or no saturated hydrocarbons.
[2] Final boiling point.

The term "hydroformate" is used herein to indicate a fraction taken from a conventional reforming operation wherein hydrogen is used in sufficient quantities to saturate any olefinic compounds but not in amounts which will affect the aromatic compounds. The term "vapor phase cracked naphtha distillate" is used herein to indicate a conventional fraction taken from a virgin naphtha gas oil, or residuum cracking operation using steam under high temperature conditions.

Ordinarily, if a saturated cut were prepared for extractive distillation, a maximum cut point of only about 85° could be used. This severely limits benzene recovery to about 83.5% as shown by the data in Table

I. Higher boiling cuts have not been taken, since prior to this invention, the higher boiling paraffins could not be successfully removed by extractive distillation. In this invention, by mixing a saturated cut having a wider boiling range having an end point in th range of 85–96° C. prior to the prefractionation, high benzene recovery, e.g., 95% of the benzene based on the mixed feed, is obtainable.

The unsaturated stock does not present the same problems as the saturated stock, since olefins and benzene are recovered in the solvent extract. Subsequent acid treatment is intended to remove substantially all of the olefinic impurities. However, as already noted, there are difficultly removable diolefins and cyclicolefins which boil close to benzene. If the unsaturated benzene feed alone is used under identical operating conditions, the purity of the solvent extract is only 95.5% at 96% recovery, whereas in the present process, the rejection of said difficultly removable olefins is accomplished by adding the hydroformate cut containing paraffins to the unsaturated stock prior to fractionation. As an example, cyclohexene which boils at 83.3° C., or within 3° C. of benzene, cannot be removed by a prefractionation step when unsaturated stocks alone are tested. By the present method, over half (55%) of the cyclohexene present in the unsaturated stock, can be removed prior to the extractive distillation step. It is to be emphasized that about twice as much of these close boiling olefins are rejected when the mixed feeds are fractionated as compared to the fractionation of the unsaturated stock alone. This results as will be explained hereinafter in reduced benzene loss during the acid treating steps. Moreover, the amount of acid treatment required to produce high grade benzene is substantially reduced as a result of the prefractionation step of this invention.

A preferred method of operation will be described with reference to the accompanying drawing in which is shown a schematic flow plan for preparing the mixed feed stock, fractionating said mixed stock, extractively distilling the mixed feed stock and thereafter recovering the purified benzene.

Referring to the drawing, essentially saturated crude benzene feed stock is supplied through line **1** to a fractionator column **2** equipped with a reflux condenser **4**. A saturated side stream benzene cut of about 60° and 96° C. is taken off through line **6**. Hydrocarbons boiling lower than benzene are withdrawn with as little benzene as practical, as the overhead product through line **5** after being refluxed at **4**. Higher boiling constituents may be taken off through line **35**. The other crude benzene feed stock, in which the impurities are mainly olefinic, such as a thermally cracked naphtha stock having a boiling range of about 33° to 143° C. is led through line **7** and mixed with the saturated stock. It is preferable to maintain the ratio of these feed stocks constant during the prefractionation. The combined feeds **8** are then led to a prefractionator tower **9** where 95% of the benzene from the combined feeds is taken off as a side stream via line **13**. Paraffins boiling above about 85° C. and difficultly removable olefins boiling close to benzene are rejected via line **12**. Lower boiling components including very minor amounts of benzene are refluxed at **10** and taken overhead via line **11**. The side stream benzene cut is then led via line **13** to extraction zone **14** and a solvent such as phenol is injected via line **19** into said zone **14**. Raffinates are taken overhead through reflux **15** out line **16** and the solvent extract is taken via line **17** and led to the stripper tower **18**. Regenerated solvent may be recycled to extraction zone **14** via line **19**. Benzene containing some olefins in an amount of from about 1 to 4 wt. percent is taken overhead through line **21** after reflux at **20**. The benzene cut at this point is then subjected to a conventional acid treatment. The following represents the composition of a typical benzene cut at this point.

	Wt. percent
Benzene	97.8
Cyclohexene	0.7
Diolefins	1.0
Olefins	.45–0.5
Paraffins	<0.06

Sulfuric acid of about 80 to 100% strength may be used in amounts of the order of 10 to 40 lbs. per bbl. of the benzene olefin distillate. The acid is added through line **34**, mixed with the solvent extract in mixer **23** and led to an acid settler **24** where the treated benzene and spent acid are separated. Acid sludge is removed as a bottom layer from vessel **24** by line **25** and treated benzene is then decanted from vessel **24** and led to line **22** wherein caustic is added via line **26**. The neutralized mixture is then led to settler **27** wherein spent caustic is withdrawn from the bottom layer by line **28**. Neutralized benzene is then decanted and passed by line **29** to the finishing fractionator **30** and benzene is recovered overhead through line **32** after refluxing at **31**. Flux oil may be added at **35** prior to fractionation. Bottoms are taken off through line **33**. The various fractionators may contain conventional reboilers. It is to be understood that the benzene cut taken from tower **13** may be used as such or it may be led to further finishing steps as above indicated.

The volume ratio of the original feed stocks to be mixed will depend upon the amounts of lower boiling constituents present in each. While it is preferred that the volume ratio of saturated stock to unsaturated stock be about 1:1 based on the lower boiling constituents, e.g., those boiling between about 49° C. to 85° C., a wide range of proportions may be used. The volume ratio of paraffin to olefin based on these lower boiling components may accordingly vary between about 1:3 and 6:1. With any choice, sufficient paraffin must be present to effect a rejection of the difficultly removable olefins in the prefractionator.

Several alternative methods which come within the scope of this invention may be used. Instead of mixing the hydroformate and cracked stock prior to distillation, both feeds may be injected into tower **9** independently. If this method is chosen, the unsaturated feed stock should be led into the tower **9** at a point above the point where the hydroformate feed is admitted. Also, the overhead product taken off at **11** may be fed back to the benzene cut anywhere along line **13** or directly to tower **14**. The following example is illustrative of a process of the present invention.

Example.—2500 barrels of hydroformate containing about 159 barrels of benzene are fractionated in a column (approximately 45 plates) at about 3 to 1 reflux ratio to obtain a 60° to 96° C. distillate.

From another source, 2200 barrels of a high temperature cracked naphtha fraction containing about 460 barrels benzene having a 33°–143° C. of boiling range is mixed with the hydroformate cut from column **2**. The resulting blend which contains about 20 vol. percent of benzene is subjected to fractionation as in tower **9**. About 1450 barrels of side stream benzene cut having a boiling range of about 60–85° C. is taken off at line **13**, said cut containing 95% of the benzene based on the combined original feeds. Tower **9** is a 48 plate tower with a reflux ratio of about 4 to 1. This side stream (**13**) contains 580 barrels of benzene at about 40 vol. percent concentration. Higher boiling paraffins, e.g., 85–96° C., are rejected as a bottom stream through line **12** and the benzene cut is then led to extractive distillation tower **14** which contains 60 plates wherein phenol is admitted through line **19**. The phenol extraction is operated at about 75 mole percent concentration with a reflux ratio of about 4 to 1. Phenol extract is then led via line **17** to a stripping tower **18** wherein the overhead temperature is maintained at about 80.1° C. The benzene is taken

overhead via line 21 at about 98% purity and 96% of the benzene in the phenol extract is recovered. The overhead product contains about 557 barrels of benzene. The benzene-olefin extract stripped from the solvent is acid treated, caustic washed, redistilled and a final benzene product of high purity is recovered. Due to the small amount of olefinic impurities in the phenol extract of about 2%, only small losses of benzene (2%) is realized in the final acid treatment. This compares favorably to the prior art processes wherein the olefinic impurities are considerably greater resulting in a higher benzene loss.

Various saturated and unsaturated feed stocks containing appreciable quantities of benzene may be used.

The composition of a typical hydroformate and thermally cracked naphthas may vary considerably as indicated in the following table:

	Hydroformate, range (wt. percent)	Thermally Cracked Naphtha, range (wt. percent)
Paraffins	30–65	0–10
Naphthenes	5–30	0–5
Aromatics	5–65	10–70
Olefins	0–4	10–75
Diolefins	nil	1–15

Major features of the process are:

(1) Blending a wide hydroformate benzene fraction and a wide cracked stock fraction prior to fractionation to permit high recovery of benzene.

(2) Easy rejection of high boiling paraffins and olefins such as cyclohexene and cyclohexadiene.

(3) Reducing the olefinic impurities in the solvent extract to permit a reduction of benzene loss during acid treatment.

(4) Reducing phenol losses and fouling in the tower by fractionation of all components immediately prior to extractive distillation.

What is claimed is:

1. A process of recovering benzene from saturated and unsaturated feed stocks which comprises mixing a saturated feed stock containing benzene contaminated with paraffins boiling within the range of 85° to 96° C. with a wide unsaturated benzene feed stock contaminated with difficultly removable olefins and diolefins having boiling

points close to that of benzene, and other higher boiling unsaturated contaminants, fractionating said mixed feed stocks to reject as a bottoms product with low benzene loss at least a substantial portion of said close-boiling olefins and diolefins, said paraffin contaminants boiling within the range of 85° to 96° C., and other contaminants boiling above about 85° C., and to recover a benzene fraction, extractively distilling said benzene fraction and recovering benzene of high purity with little benzene loss.

2. A process in accordance with claim 1 wherein the extract from the extractive distillation step contains about 1 to 4 weight percent olefin impurities.

3. A process in accordance with claim 1 wherein said freshly distilled benzene fraction is extractively distilled without substantial delay.

4. A process in accordance with claim 1 wherein said difficultly removable olefins having boiling points close to benzene include cyclohexene and cyclohexadiene.

5. In a process of recovering benzene from mixed feed stocks, the steps which comprise admixing a saturated feed stock containing benzene and some difficultly removable paraffins, said saturated stock having a boiling range of about 60–96° C., with an unsaturated feed stock containing benzene and difficultly removable olefinic compounds, said unsaturated stock boiling between about 33°–160° C., fractionating the mixed feed stocks to recover a benzene fraction having a boiling range of about 60–85° C., at about 95% benzene recovery based on the mixed feed stocks, extractively distilling said fraction to recover a benzene extract substantially free of saturated impurities and containing a maximum of olefinic impurities up to about 4 wt. percent.

6. A process in accordance with claim 5 wherein said freshly distilled benzene fraction having a boiling range of about 60–85° C., is extractively distilled without substantial delay to avoid phenol losses and fueling difficulties.

7. A process in accordance with claim 5 wherein said difficultly removable olefins include cyclohexene and cyclohexadiene.

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