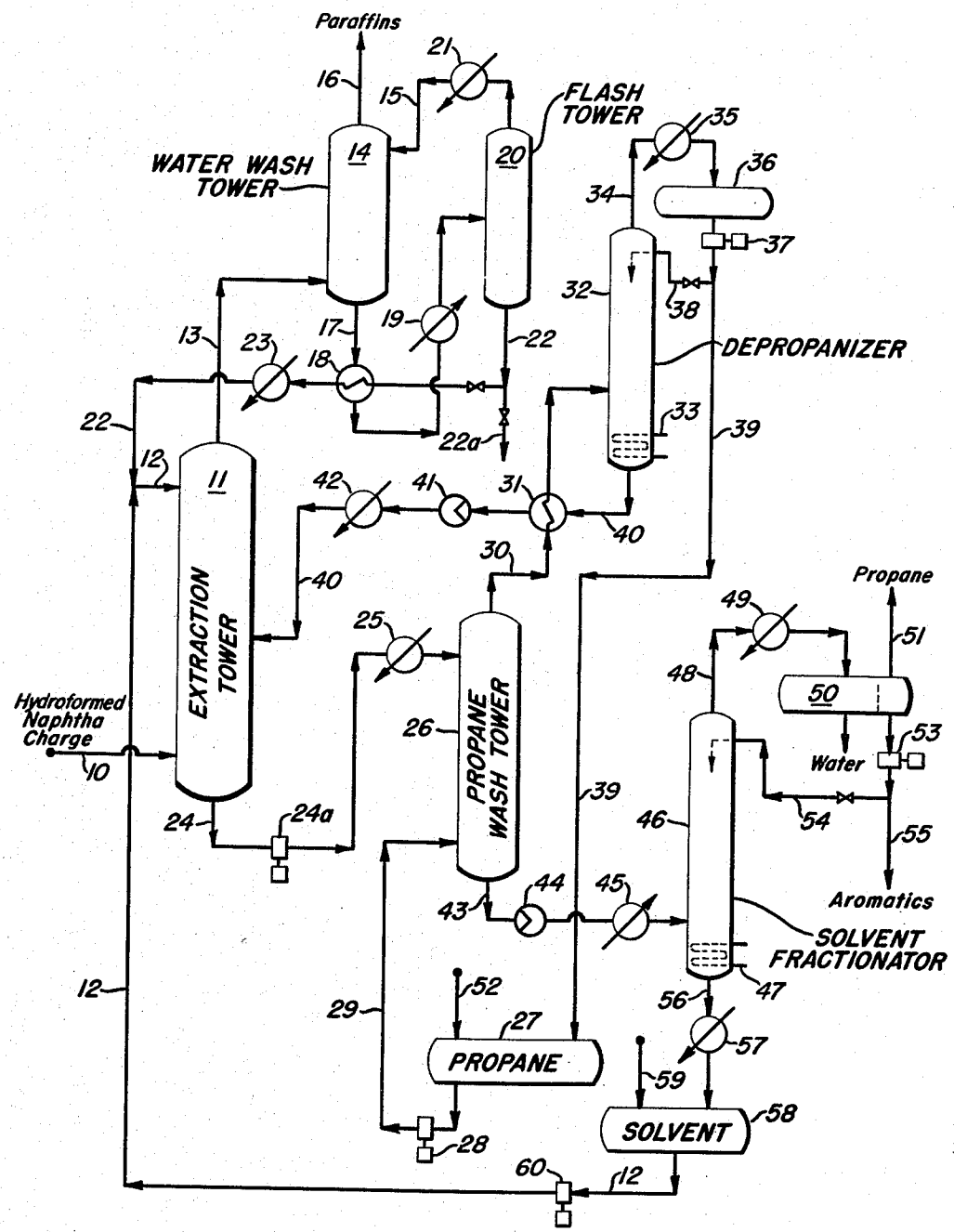
Dec. 6, 1960 T. D. NEVITT 2,963,427

AROMATICS RECOVERY SYSTEM USING BUTYROLACTONE IN THE FIRST STAGE AND PROPANE IN THE SECOND STAGE

Filed April 18, 1956



INVENTOR.
Thomas D. Nevitt

BY Donald C. Payne

ATTORNEY

United States Patent Office 2,963,427 Patented Dec. 6, 1960

2,963,427

AROMATICS RECOVERY SYSTEM USING BUTYROLACTONE IN THE FIRST STAGE AND PROPANE IN THE SECOND STAGE

Thomas D. Nevitt, Crown Point, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Filed Apr. 18, 1956, Ser. No. 578,999

3 Claims. (Cl. 208—315)

This invention relates to an improved system for recovering aromatics from hydroformed naphtha and it pertains more particularly to an improved extraction system employing a selective solvent such as gamma butyrolactone in a first stage and a countercurrent washing of solvent extract with a normally gaseous paraffinic hydrocarbon such as propane in a second stage.

Extraction of hydrocarbon oils with selective solvents is an old and well known technique, its most extensive commercial use having been for the separation of so-called naphthenic components from paraffinic components of lubricating oil stocks. In recent years there has been a phenomenal increase in the use of hydroforming for upgrading the anti-knock properties of naphthas and for obtaining relatively pure aromatics such as benzene, toluene, xylenes, etc. useful in the petrochemical field. The recovery of aromatics from hydroformed naphthas presents problems not encountered in lubricating oil extraction since it requires the use of different types of solvents under different conditions and the use of different solvent recovery techniques. The object of my invention is to provide an improved system for separating relatively low boiling aromatics from hydroformed naphtha. A more specific object is to provide a system which will minimize solvent losses while at the same time insuring sharper fractionation between aromatics and paraffins than has heretofore been obtainable. A further object is to obtain a substantially complete separation of low boiling aromatics from paraffins with minimum investment and operating cost. Other objects will be apparent as the detailed description of the invention proceeds.

While many solvents may be employed for extracting aromatics from hydroformed naphtha, an aqueous polyethylene glycol solvent being the one most widely used on a commercial basis, it has been found that butyrolactone has unusual and remarkably effectiveness for this purpose. With a solvent to hydrocarbon ratio of about 1.5:1 in an efficient countercurrent system at about 25° C., it will remove substantially all of the aromatics from a hydroformed naphtha but the solvent extract phase will contain substantial amounts of paraffinic hydrocarbons. If ratios and conditions are employed for increasing the purity of the aromatics in the extract (pure aromatics cannot thus be obtained), then large amounts of the aromatics are lost in the raffinate phase. Even by employing large solvent to oil ratios, cooling the extract to very low temperatures, and/or employing water to increase the selectivity of the extract, it is difficult and expensive to obtain paraffin-free extract simultaneously with aromatic-free raffinates.

In accordance with my invention the hydroformed naphtha is first countercurrently extracted with a selective solvent of high capacity such as gammo butyrolactone under conditions to remove substantially all aromatics along with a portion of the paraffins contained in the naphtha. The extract phase is then countercurrently washed with liquid propane in amounts of about .2 to 5, preferably .5 to 2, volumes per volume of solvent extract

under conditions to remove substantially all paraffins as a second raffinate. The substantially pure aromatics are distilled from the solvent and the solvent is then returned to the initial extraction step, the small amount of propane being separated from solvent in this distillation step. Propane is removed from the second raffinate at high pressure so that it may be re-employed without compression and the second raffinate, including solvent contained therein, is returned at an intermediate point in the initial extraction zone. The first raffinate may be simply water-washed to remove solvent, the wash water being flashed to separate wash water from removed solvent, although the paraffins may be distilled from the solvent in the same way that aromatics are distilled therefrom. Advantageous results may be obtained by using butane or other normally gaseous hydrocarbon instead of propane and/or by effecting the extraction in a single tower into which the naphtha is introduced at a mid point, the propane at the base and the solvent at the top, using the usual fractionation methods for recovering and recycling propane and solvent; this technique is not to be construed, however, as the equivalent of extract washing in a separate tower.

Re-extraction of a primary extract with a secondary solvent or counter solvent is an old technique, particularly in lubricating oil extraction, but these prior processes were not effective for obtaining substantially complete separation of paraffins from aromatics without undue expense. In my preferred process it is only necessary to separate propane from secondary raffinate since the butyrolactone contained in this raffinate is returned to the initial extraction tower. Simple distillation suffices to separate propane, water (if present) and aromatics from solvent in the second extract, a depropanizer being employed in addition to the final distillation step if desired. In an extensive test program on the use of various hydrocarbon extractants for washing the first raffinate, I have found propane to be remarkably superior to butanes and normally gaseous hydrocarbons superior to pentanes and hexanes.

The initial extraction step is preferably effected with gamma butyrolactone at a temperature in the range of about 50° C. to −30° C., preferably at about 0° C. to 25° C. with a solvent to oil ratio in the range of about .5:1 to 3:1, preferably about 1.5 to 2:1. The propane washing of the first extract is preferably effected at a lower temperature than the first extraction step and is preferably effected at about −20° C. to 0° C. although other temperatures in the range of −40° to +40° C. may be employed. The amount of propane required in the washing step will depend upon the efficiency of the countercurrent wash tower and the washing temperature, less amounts of propane being required at lower temperatures. About .5 to 2 volumes of propane per volume of first extract is usually adequate to obtain aromatics of desired purity in an efficient countercurrent contacting system. It should be understood that the term propane is intended to mean a technical grade of propane, i.e. a hydrocarbon of approximately the propane boiling range, even though said hydrocarbon contains small amounts of propylene, butanes, etc. The gamma butyrolactone is preferably anhydrous in order to avoid separation difficulties caused by azeotropes, but amounts of water up to 10 percent or more may be used.

The invention will be more clearly understood from the accompanying drawing which is a schematic flow diagram of my improved extraction process.

In this example the charging stock is a 300° F. end point light naphtha obtained by the fractionation of a naphtha which has been hydroformed over platinum-alumina catalyst by the Ultraforming process ("Ultraforming," Oil and Gas Journal, March 21, 1955, vol. 53,

No. 46, pages 160–161). Such hydroformed light naphtha is introduced by line **10** at the base of extraction tower **11** wherein the charge is countercurrently contacted at about 25° C. with 1½ volumes of butyrolactone introduced at the upper part of the tower through line **12**. Extraction tower **11** may be provided with suitable packing, baffles or other known means for obtaining efficient countercurrent contact. First raffinate is removed from the top of the tower by line **13** and introduced into wash tower **14** wherein it is scrubbed with water introduced by line **15** for removing the small amount of solvent which is contained therein. The solvent-free raffinate withdrawn from line **16** consists essentially of paraffins and is substantially free from aromatic hydrocarbons. The wash water leaves the base of tower **14** through line **17**, heat exchanger **18** and heater **19** and it is flashed or fractionated in tower **20** to separate water from solvent, the water being condensed in exchanger **21** and returned to the upper part of wash tower **14** and the solvent being either returned by line **22**, heat exchanger **18** and cooler **23** for introduction through line **12** to extraction tower **11** or introduced by line **22***a* to the solvent storage tank.

The first extract which leaves the base of tower **11** through line **24** is pumped by pump **24***a* to a pressure of 200 to 500 p.s.i.g., e.g. about 300 p.s.i.g., and introduced through cooler **25** to the upper part of propane wash tower **26** at a temperature of about 0° C. An amount of propane from storage tank **27** is introduced at the base of tower **26** by pump **28** and line **29** to provide about 2 volumes of wash liquid per volume of extract, the propane likewise being introduced at a temperature of approximately 0° C. Tower **26**, like tower **11**, may be provided with suitable packing, baffles or other known means for obtaining efficient countercurrent contact.

The second raffinate leaves the top of tower **26** through line **30** and heat exchanger **31** and is introduced into depropanizer **32** which is provided with the usual heater or reboiler **33** at its base. Propane is taken overhead through line **34** and condenser **35** to receiver **36**, a part of the condensate from the receiver being returned by pump **37** and line **38** to serve as reflux in the depropanizer and the remainder of the propane being returned by line **39** to propane storage tank **27**, the temperature of which may be maintained at about 0° C. The depropanized second raffinate leaves the base of depropanizer **32** through line **40** and is passed through heat exchanger **31**, pressure reducing valve **41** and cooler **42** to a low point in extraction tower **11** or to naphtha inlet line **10**. Since there is a wide spread between the boiling point of propane and the lowest boiling component of the light naphtha, it is a simple matter to separate substantially all propane from the solvent and hydrocarbon mixture which is returned by line **40** to the initial extraction tower.

The second extract withdrawn through line **43** from wash tower **26** passes through pressure reducing valve **44** and heater **45** to fractionator **46** which may be provided with conventional reboiler means **47**. In tower **46** the aromatic hydrocarbons together with the slight amount of propane which is carried over by the extract are taken overhead through line **48** and cooler **49** to receiver **50** from which uncondensed propane many be removed through line **51**; this propane may be compressed and returned to storage tank **27** but it is preferably introduced to the usual refinery vapor recovery units and makeup propane is supplied to storage tank **27** by line **52**. A part of the aromatics may be returned by pump **53** and line **54** to serve as reflux in fractionator tower **56** and the final aromatic product is removed through line **55**. This aromatic product is substantially free from paraffinic hydrocarbons other than propane and although it may contain a small amount of dissolved propane, such propane may readily be removed therefrom by the subsequent fractionation system in which closely fractionated aromatics are obtained for use in petrochemical processes or by a depropanizer if the aromatics are to provide high octane number gasoline components. When butane is used as the wash liquid for preparing high octane motor fuel blending stock, the removal of the butane from the extract may be unnecessary.

The solvent removed from the base of fractionator **46** through line **56** is cooled to about 35° C. by heat exchanger **57** and introduced into storage tank **58**, makeup solvent being introduced as required through line **59**. The solvent is supplied from storage tank **58** by pump **60** to line **12**.

To demonstrate the remarkable effectiveness of normally gaseous hydrocarbons such as propane for washing paraffins out of extract, a series of tests were made with different hydrocarbon wash liquids on a synthetic "extract" containing 73 volumes of toluene (aromatic), 27 volumes of isooctane (paraffin) and 200 volumes of gamma butyrolactone (solvent). This extract was mixed with an equal volume of hydrocarbon to be tested as a wash liquid, the mixture was agitated at about 77° F. to obtain intimate contacting, the phases were then separated and the two phases analyzed to determine the percent of hydrocarbons washed out of the extract, the aromatic-to-paraffin ratio in the hydrocarbons washed out and the aromatic-to-paraffin ratio in the final extract subsequently recovered from the solvent. The following data were obtained:

Wash Liquid	Percent of Hydrocarbons Washed from Extract	Aromatic to Paraffin Ratio of Raffinate	Aromatic to Paraffin Ratio of Final Extract	Percent Aromatics in Final Extract
Propane	74	2.3	20.7	95+
Isobutane	60	1.5	10.7	91+
N-butane	60	1.4	9.0	90
Isopentane	62	1.8	7.3	88
Diisopropyl (a hexane)	53	2.3	4.2	81

The foregoing data show that propane is outstandingly superior to other normally gaseous hydrocarbons as a wash liquid, that propane may be used in smaller amounts than other hydrocarbon wash liquids and that the use of propane gives aromatics of much higher purity than are attainable with other hydrocarbon wash liquids. In a countercurrent wash system 1 volume of propane wash liquid may effectively remove substantially all paraffins from the extract. While butane (either iso or normal) is inferior to propane as a wash liquid, it is more effective than isopentane or the hexane (diisopropyl) tested. Furthermore, the normally gaseous hydrocarbons such as propane can be more readily separated from second raffinate than normally liquid paraffinic wash liquids. When 3.8 volumes of the synthetic extract was similarly washed with 1 volume of propane, 43 percent of the hydrocarbons were washed out of the extract, the aromatic-to-paraffin ratio of the removed hydrocarbons was approximately 1:1 and the aromatic-to-paraffin in the final extra was 10:1, indicating that even with this inefficient contacting system an aromatic purity greater than 90 percent was obtained.

While a particular example of my invention has thus been described in considerable detail, it should be understood that alternative arrangements, steps and conditions will be apparent from said description to those skilled in the art. A depropanizer (corresponding to tower **32**) may be interposed in line **43**, prior to reduction of pressure by valve **44**, in which case the propane is returned to the storage vessel **27** and only aromatics (and perhaps water) are removed from solvent in fractionator **46**.

If appreciable amounts of water are contained in the solvent, such water is separated from condensed aromatics

and withdrawn from receiver **50**. An advantage of my system is that it does not require the use of water for improving the selectivity of the solvent so that the full capacity of the solvent as an extractant may be utilized in the initial extraction stage and the effect of selectivity is enhanced by the washing of the extract with normally gaseous hydrocarbon such as propane. To minimize water in the extraction system, water may be distilled from solvent instead of merely being flashed therefrom in tower **20**.

The invention is directed particularly to the use of gamma butyrolactone as the selective solvent, but advantageous results may also be obtained by the use of other solvents having a high capacity and selectivity for low boiling aromatics and also having the required stability and high boiling point, provided that the extraction conditions be modified to meet the requirements of the particular solvent.

I claim:

1. The method of effecting substantially complete separation of a light naphtha consisting chiefly of aromatic and paraffinic hydrocarbon into a substantially pure aromatic hydrocarbon fraction and a paraffinic hydrocarbon fraction substantially free from aromatic hydrocarbon, which method comprises countercurrently extracting said naphtha in the liquid phase in a first extraction zone with about .5 to 3 volumes of butyrolactone per volume of naphtha at a temperature in the range of about −30° C. to +50° C. to obtain a first liquid raffiniate of paraffinic hydrocarbons substantially free from aromatic hydrocarbons and a first liquid extract containing aromatic and paraffinic hydrocarbons, removing butyrolactone from said first liquid raffinate, countercurrently washing said first liquid extract with about .5 to 5 volumes of liquid propane per volume of first liquid extract at a temperature in the range of −40° to +40° C. and under a pressure of about 200 to 500 p.s.i., separating a second liquid extract which is substantially free from paraffinic hydrocarbons of the naphtha boiling range and a second liquid raffinate containing substantinally all of the paraffins from said first liquid extract, distilling propane and aromatic hydrocarbon from said second liquid extract as separate fractions, recovering said aromatic hydrocarbon from the distillation as substantially pure aromatic hydrocarbon, depropanizing said second liquid raffinate without any substantial reduction in pressure, recycling propane thus obtained to the propane washing step and returning depropanized second liquid raffinate containing both butyrolactone and paraffins to an intermediate level in the first extraction zone.

2. A method of liquid-liquid solvent extracting a light naphtha consisting chiefly of aromatic and paraffinic hydrocarbons, which method comprises countercurrently contacting one volume of said naphtha in the liquid phase with about .5 to 3 volumes of anhydrous butyrolactone solvent in a first extraction zone at a temperature of about 25° C., separating a first liquid extract containing aromatic and paraffinic hydrocarbons and a first liquid raffinate of paraffinic hydrocarbons substantially free from aromatic hydrocarbons as separate countercurrent liquid phases from said first extraction zone, removing butyrolactone solvent from said first liquid raffinate, countercurrently washing said first liquid extract with about .5 to 5 volumes of normally gaseous propane in the liquid state per volume of first liquid extract at a temperature of about 0° C. and under a pressure of about 200 to 500 p.s.i., separating from said washing step a second liquid extract containing aromatic hydrocarbons substantially free from paraffinic hydrocarbons of the naphtha boiling range and a second liquid raffinate containing substantially all of the paraffins from said first liquid extract, distilling propane and aromatic hydrocarbon from said second liquid raffinate as separate fractions, recovering said aromatic hydrocarbon from the distillation as aromatic hydrocarbons of 95+% purity, depropanizing said second liquid raffinate without any substantial reduction in pressure from said about 100 to 500 p.s.i., recycling propane from the depropanizing step to the propane washing step and returning depropanized second liquid raffinate containing both butyrolactone and paraffins to an intermediate level in the first extraction zone.

3. The method of claim 1 which includes the step of washing the first raffinate with water to remove solvent therefrom, fractionating the solvent-containing wash water to separate water from solvent and returning the separated solvent to the first extraction step.

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