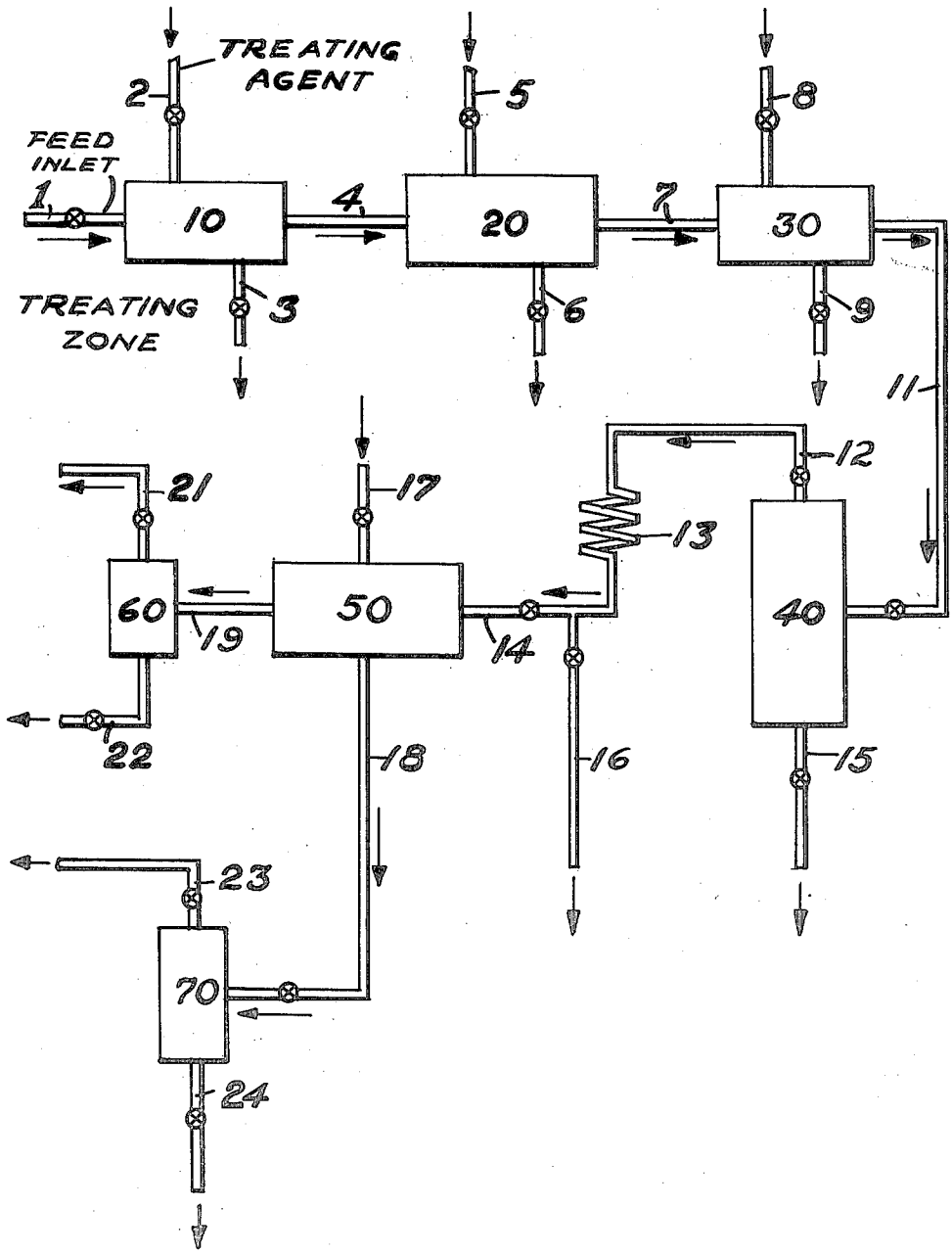
Sept. 25, 1951 E. ARUNDALE 2,569,216

SEPARATION OF OLEFINS FROM HYDROCARBON DISTILLATES CONTAINING AROMATICS

Filed April 15, 1949



Erving Arundale Inventor

By W. O. Tilman Attorney

Patented Sept. 25, 1951

2,569,216

UNITED STATES PATENT OFFICE

2,569,216

SEPARATION OF OLEFINS FROM HYDROCARBON DISTILLATES CONTAINING AROMATICS

Erving Arundale, Westfield, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application April 15, 1949, Serial No. 87,664

2 Claims. (Cl. 260—674)

1

The present invention is concerned with the selective removal of olefinic compounds from hydrocarbon fractions containing the same. The invention is more particularly concerned with the segregation of olefin type compounds from aromatic hydrocarbons in order to produce a product having a high aromatic content. In accordance with the preferred adaptation of the present invention, product streams substantially completely free, or having a relatively low olefin content are secured by contacting the feed streams with a relatively dilute acid in conjunction with an aldehyde. A particularly desirable adaptation of the present invention is to contact an aromatic type feed stream containing olefins with a relatively dilute sulfuric acid together with a small amount of formaldehyde.

It is well known in the art that various types of hydrocarbon constituents can be segregated from other types by utilizing a chemical reagent which will react with the one type only. For example, it has been proposed in the art to separate various olefinic type constituents from hydrocarbon fractions by treating a mixture containing the same with formaldehyde, and using in conjunction therewith an acid; as for example, concentrated sulfuric acid. In this so-called "Formalite" reaction, concentrated sulfuric acid, hydrochloric acid, or Friedel-Crafts type catalysts are employed in conjunction with formaldehyde in order to segregate and remove olefinic type hydrocarbons. However, when acids of this concentration are utilized the aromatic hydrocarbons also condense with the aldehydes to form di-aryl methane type compounds as well as their sulphonates and various resins. It has now, however, been discovered that a selective separation between aromatic type constituents and olefinic constituents can readily be secured providing a relatively dilute acid is employed in conjunction with an aldehyde. By operating in this manner the aldehyde reacts only with the olefinic and polydiolefinic hydrocarbons and apparently does not react to any measurable degree with the aromatic type constituents. Thus, it is possible by the present process to secure high yields of aromatic type products, which products contain a relatively small concentration of undesirable olefinic compounds.

The present invention may be readily understood by reference to the drawing illustrating one embodiment of the same. Referring specifically to the drawing, a feed stream which for the purpose of illustration is assumed to comprise aromatic type constituents and olefinic compounds boiling in approximately the same boiling range is introduced into treating zone 10, by means of feed line 1. An acid which for the purpose of illustration is assumed to be a dilute sulfuric acid, together with a relatively small concentration of an aldehyde, as for example formaldehyde, is introduced into zone 10 by means of line 2. Temperature, pressure and mixing conditions in zone 10 are adjusted to secure the desired removal of the olefinic type constituents. In general the temperature in zone 10 is in the range from about 20° C. to 50° C. The spent acid, or treating agent is withdrawn from zone 10 by means of line 3 and may be regenerated or recycled. It is to be understood that a zone may comprise any suitable number and arrangement of treating stages. Furthermore, it is to be understood that any means may be employed to secure the desired contact between the treating agent and the feed stream being contacted.

2

The treated hydrocarbon fraction containing aromatic type constituents and olefinic-aldehyde complexes is withdrawn from zone 10 by means of line 4 and introduced into treating zone 20 wherein the same is preferably contacted with an alkali solution. The alkali solution which for the purpose of illustration is assumed to be a 5% sodium hydroxide solution, is introduced into zone 20 by means of line 5 and withdrawn by means of line 6. Here again zone 20 may comprise any suitable number and arrangement of treating stages. Satisfactory contacting and mixing means are also utilized. The caustic washed hydrocarbon stream is removed from zone 20 by means of line 7 and introduced into zone 30 wherein the same is washed with water which is introduced into zone 30 by means of line 8 and withdrawn by means of line 9.

The water washed hydrocarbon fraction is withdrawn from zone 30 by means of line 11 and introduced into distillation zone 40. Temperature and pressure conditions are adjusted in zone 40 so as to distill overhead, by means of line 12, a fraction boiling substantially within the boiling range of the feed fraction. This overhead stream is passed through a condensing zone 13 and is withdrawn from the system by means of line 14. The heavier boiling fraction boiling above the boiling range of the feed fraction which comprises olefinic-aldehyde complexes is withdrawn from the bottom of zone 40 by means of line 15

and may be used as a chemical raw material or solvent with or without further distillation or purification.

If the feed stream also contained paraffinic type constituents, these paraffinic hydrocarbons will be present with the aromatic constituents removed by means of line 14. It is, therefore, within the concept of the present invention to withdraw aromatic type constituents from the system by means of line 16 if no paraffins are present in the feed stream introduced into zone 10, or if the paraffinic-aromatic fraction is to be desired. However, if the feed stream contains paraffins and it is desired to secure a relatively pure aromatic type product, the overhead distillate stream, removed from condenser 13 by means of line 14 is introduced into a solvent treating zone 50.

In zone 50 the stream containing aromatics and paraffins is contacted at substantially room temperature with a solvent which has a preferential selectivity for the more aromatic type compounds as compared to the more paraffinic type constituents. This solvent is introduced into zone 50 by means of line 17 and is withdrawn by means of line 18. Satisfactory solvents are for example, phenol, liquid sulfur dioxide, furfural, and the like. These solvents may also contain various solvent modifying agents, as for example, water or liquefied normally gaseous hydrocarbons. It is to be understood that zone 50 may comprise any suitable number and arrangement of treating stages. Zone 50 may also comprise a countercurrent solvent treating operation. It is also to be understood that any suitable distributing and contacting means may be employed in the solvent treating process. The stream comprising essentially paraffinic hydrocarbons is withdrawn from zone 50 by means of line 19 and introduced into zone 60 where any residual selective solvent is substantially completely removed from the paraffinic type constituents by distillation or washing. If sulfur dioxide is used, the small amount of residual solvent is removed overhead on distillation by means of line 21 while the paraffinic constituents are removed as a bottom stream by means of line 22.

In a similar manner the selective solvent solution of the aromatic type constituents removed from zone 50 by means of line 18, is introduced into solvent recovery zone 70 where temperature and pressure conditions are adjusted to remove overhead the selective solvent by means of line 23, and to remove as a bottoms, by means of line 24, a stream comprising essentially pure aromatic type compounds. The solvent may be recycled to zone 50 if so desired.

The present invention is broadly concerned with the removal of olefinic type constituents from hydrocarbon fractions containing the same. It is particularly adapted for use when the olefinic type constituents boil in substantially the same boiling range as other hydrocarbon constituents particularly aromatics from which it is desired to segregate the same. An especially desirable adaptation of the present process is for the production of product streams having a high aromatic content. As pointed out heretofore, various proposals have been suggested where a chemical reagent is employed which reacts with the olefinic type constituents to form a complex. Reagents which have been suggested are for example concentrated acids, such as sulfuric acid, hydrochloric acid, and Friedel-Crafts type catalyst used as such or in conjunction with an aldehyde. However, these acids, and other catalysts all react, at least to some degree with the aromatic compounds thus substantially decreasing the yield of the desired product. However, if the acid strength is maintained at a relatively low level, and the aldehyde concentration is controlled with respect to the olefins present, it has been found that a high degree of removal of the olefins can be secured without substantially affecting the aromatic constituents present.

The present invention may be used in the treatment of streams which contain only aromatics and olefins. The invention can also be used for treating hydrocarbon distillates secured in petroleum refining operations which contain aromatic and olefinic or di-olefinic hydrocarbons. These distillates may be obtained, for example, from refinery steam cracking, aromatization, or hydroforming processes. The invention may be employed in the treatment of feed streams boiling over a wide boiling range. It is, however, best adapted to those fractions boiling below about 700° F., at atmospheric pressure and particularly those fractions boiling in the motor fuel boiling range (80° F. to 430° F.). It is particularly adapted in the treatment of a feed stream boiling in the range from about 150° to 300° F., secured in a petroleum cracking operation wherein a product stream having a relatively high concentration of aromatics and olefins is present.

The acid employed in the present invention may be any dilute aqueous solution of an inorganic acid, as for example, sulfuric acid, phosphoric acid, or hydrochloric acid. However, the preferred acid comprises dilute sulfuric acid which has a concentration not in excess of about 80% by weight and not below 50% by weight. The preferred concentration of the acid to be employed is in the range from about 60% to 70%.

Any aldehyde may be employed, as for example, acetaldehyde, propinaldehyde, butyraldehyde, benzaldehyde or acrolein. However, the preferred treating agent comprises formaldehyde or a compound which will yield formaldehyde under the treating conditions as for example trioxane or methylal. A particularly desirable form of formaldehyde is its aqueous solution called Formalin (37% formaldehyde in water). Paraformaldehyde likewise may be employed (approximately 94% formaldehyde, 5% methanol and 1% water). The concentration of the aldehyde used is such that between 1.5 and 2.5 mols of aldehyde is present per mol of olefin in the feed.

The quantity of treating solution used (aldehyde and acid) may be varied appreciably depending upon the character of the feed oil being contacted. However, in general it is preferred that from about 5% to 25% by volume of treating solution be used based upon the feed stream being contacted.

The temperature of treating may be varied appreciably, but it is preferred that this temperature be in the range from about 20° C. to about 50° C. It is to be understood that when the concentration of the acid utilized is specified, it is specified with respect to the total water present irrespective as to the source of the water.

In a commercial operation the aldehyde can be added to the oil and the mixture then contacted with the acid, or the aldehyde can be added directly to the acid and this solution utilized to contact the oil.

It is possible also to remove olefinic hydrocarbons from distillates containing aromatics by heating the distillate with Formalin solution or

paraformaldehyde under pressure at temperatures between 150°–300° C. in the absence of added catalysts and subsequently distilling the treated product to separate the aromatic hydrocarbons therefrom.

The present invention may be more fully understood by the following example illustrating embodiments of the same.

EXAMPLE

Five operations were conducted wherein various mixtures of aromatics and olefins were contacted with sulfuric acid having a concentration of 65 weight per cent. Other operations were also conducted wherein the conditions were similar except that various concentrations of formaldehyde were employed in conjunction with the acid. The operations wherein only the acid was employed are listed as operations 1 to 5 in Table A whereas the operations wherein the aldehyde was used in conjunction with the acid are listed as 1A to 5A inclusive.

In these operations 250 grams of a 90–10 weight percent aromatic-olefin blend were contacted, at room temperature, for two hours with (*a*) 20% (vol.) of a 65% (weight) sulfuric acid solution alone and (*b*), with 20% (vol.) of a 65% (weight) sulfuric acid solution to which paraformaldehyde had been added in amount equal to two mols of formaldehyde per mol of olefin present in the feed blend. The lower acid layer was then separated and the upper organic layer washed with a 5% sodium hydroxide solution to neutralize traces of acid. After neutralization the product was water washed, filtered to remove traces of water, and finally fractionated. The product cut was taken in a range from 1° C. below the boiling point of the lowest boiling feed component to 1° C. above the boiling point of the highest boiling feed component. The olefin condensation products remained behind in the still. The distillates as well as the feed blends were submitted for bromine number determination to establish their olefin contents.

The references of the various operations are listed in the following table:

TABLE A

Removal of olefins from aromatic-olefin blends

[20 Volume per cent 65% H_2SO_4 used in all runs. Treating conditions: 2 hours at room temperature.]

Operation	Feed (% by weight)	Treating Agents [1]	Distillation [2]		Bromine Numbers on [3]	
			Range	Most of Product off	Feed	Distillate
			°C.	°C.		
1	90% benzene (B. P. 80.1° C.) 10% cyclohexene (B. P. 83° C.)	65% acid alone	79–84	80.8–81	18.6	18.5
1A		65% acid + 19.5 gm. CH_2O	79–84	81.0–81.5	18.6	4.7
2	90% toluene (B. P. 110.8° C.) 10% octene-1 (B. P. 123° C.)	65% acid alone	110–124	108–111	9.7	9.3
2A		65% acid + 14.2 gm. CH_2O	110–124	108–111	9.7	5.7
3	90% toluene (B. P. 110.8° C.) 10% vinyl cyclohexene (B. P. 128° C.)	65% acid alone	110–129	109–111	22.3	19.2
3A		65% acid + 14.8 gm. CH_2O	110–129	107–111	22.3	1.1
4	90% mixed xylenes (B. P. 137–140° C.) 10% vinyl cyclohexene (B. P. 128° C.)	65% acid alone	127–141	129–140	22.1	25.3
4A		65% acid + 14.8 gm. CH_2O	127–141	131–139.5	22.1	3.9
5	90% mixed xylenes (B. P. 137–140° C.) 10% styrene (B. P. 146° C.)	65% acid alone	136–147	126–140	15.4	9.1
5A		65% acid + 15.3 gm. CH_2O	136–147	138–140	15.4	5.0

[1] 250 gms. olefin-aromatic hydrocarbon blend used in all experiments. CH_2O added as paraformaldehyde (94% CH_2O).
[2] Range = boiling range of cut taken for analysis. Most of product off = Range in which most of product distilled.
[3] Cg. Br./gm. by actual analysis.

From the foregoing it is apparent that the addition of formaldehyde to a 65% sulfuric acid solution results in a definite reduction in the olefin content of aromatic-olefin blends which cannot be obtained when treating the blend with the sulfuric acid solution alone under the same conditions.

Having described the invention it is claimed:

1. Process for the segregation of olefins from C_6 to C_8 aromatic hydrocarbons, said olefins boiling in approximately the same boiling range as the said aromatic hydrocarbons whereby the segregation cannot be made by distillation, which comprises contacting said aromatic hydrocarbons and olefins with 5 to 25 volume percent of a treating agent consisting of sulfuric acid having a concentration of 50% to 80% and an aldehyde selected from the group consisting of formaldehyde and acetaldehyde wherein the aldehyde concentration is the equivalent to about 1.2 to 2.5 mols per mol of olefin present in the aromatic hydrocarbons treated, said contacting being conducted at a temperature in the range from about 20° C. to 50° C., and subsequently distilling the said treated hydrocarbons, removing aromatic hydrocarbons as an overhead product.

2. The process defined by claim 1 in which the said aldehyde is formaldehyde and the said acid concentration is in the range of 60% to 70%.

ERVING ARUNDALE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,483,835	Ramage	Feb. 12, 1924
1,679,093	Miller et al.	July 31, 1928
2,386,055	Mottern	Oct. 2, 1945
2,415,171	Horeczy	Feb. 4, 1947
2,447,479	Salt	Aug. 17, 1948
2,454,467	Love	Nov. 23, 1948