

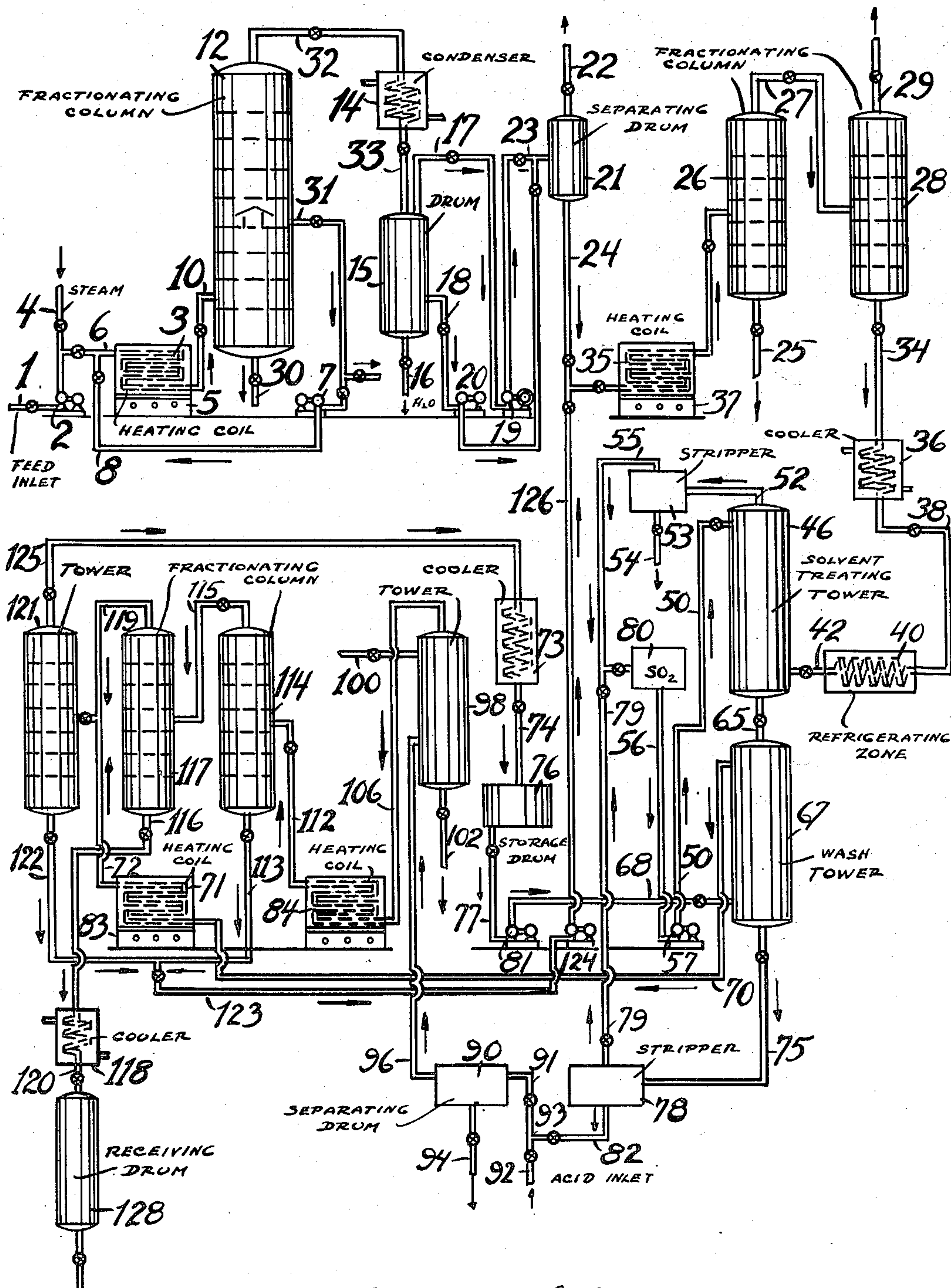
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PRODUCTION OF AROMATICS BY THERMAL CRACKING

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PRODUCTION OF AROMATICS BY THERMAL
CRACKING

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The present invention relates to improvements in the production of aromatics, including toluene, from non-benzenoid hydrocarbons, and more particularly it relates to processes for producing nitration grade toluene, entirely satisfactory for the manufacture of tri-nitro toluene, by cracking a paraffinic or naphthenic gas oil under certain specified conditions, fractionating the cracked products, recovering a fraction boiling within the range of from 200°–250° F. and subjecting the latter fraction to solvent extraction to recover the desired aromatic. By practicing our invention according to the present disclosure, we have been able to secure toluene having a purity greater than 99 per cent, or, in other words, we have secured toluene of nitratable grade.

One object of our invention, therefore, is to crack a gas oil thermally, preferably a gas oil having an end boiling point not above approximately 850° F. and containing a preponderance of paraffinic and/or naphthenic constituents.

Another object of our invention is to thermally crack gas oil in a relatively short period of time at a high temperature, thereafter to fractionate the cracked products and to recover a fraction boiling within the range of from about 200°–250° F. and thereafter selectively dissolving from this fraction very pure toluene which may be separated from the solvent in known manner.

Another object of our invention is to produce aromatic hydrocarbons from non-benzenoid hydrocarbons.

Other and further objects of our invention will appear from the ensuing description and claims, reference being had to the accompanying drawing.

The drawing represents schematically a system or combination of apparatus elements in which our invention may be carried into effect.

Referring in detail to the drawing, a gas oil having an A. P. I. gravity of about 33° and boiling within the range of from about 500° to 750° F. was introduced into the system through line 1 and pump 2 into line 6 in which this material was combined with approximately 80 mol per cent of steam based on the mixture of steam and hydrocarbons introduced through line 4, thence discharged into a coil 3 disposed in a furnace setting 5 where the feed stock was heated to a temperature of about 1200° F. while maintaining a pressure of about 8 lbs./sq. in. gauge, and in which the feed rate to the coil was about 0.5 volume of cold oil per volume of coil per hour. The oil was permitted to remain in the coil for a

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period of 2.7 seconds. Under the conditions specified, it later turned out, as will more fully appear hereinafter, that this operation resulted in the production of 45 per cent aromatics in the gasoline. The cracked products were withdrawn from coil 3 through line 10 and thence discharged into a fractionating column 12. A heavy fraction suitable for use as a fuel oil was withdrawn from fractionating column 12 through line 30 and a gas oil fraction through line 31. This gas oil may be recycled to line 6 by pump 7 and line 8, but we have found this material to be a less satisfactory charge stock than virgin materials and prefer to dispose of this fraction elsewhere. The gasoline and gaseous fractions were withdrawn from the top of column 12 through line 32, thence through condenser 14 and to separating drum 15 by means of line 33. Water was separated in drum 15 and withdrawn through line 16. Gas was removed from separating drum 15 through line 17 and gasoline through line 18, each being compressed or pumped to about 150 lbs./sq. in. gauge by means of compressor 19 and pump 20, after which these fractions were combined in line 23 and discharged into separating drum 21. This compression was necessary to recover the small quantities of aromatics contained in the gas fraction separated in drum 15 at atmospheric pressure. Gas was withdrawn from separating drum 21 through line 22 and the distillate through line 24 into coil 35 disposed in furnace setting 37, following which the vapors were fractionated in column 26. Material boiling above approximately 250° F. and free of toluene was withdrawn through line 25 and the overhead fraction containing toluene was transferred through line 27 into fractionating column 28. Materials boiling below approximately 200° F. and free of toluene were withdrawn through line 29 and the crude toluene-containing fraction through line 34. The gaseous fractions leaving the system through lines 22 and 29 were found to be rich in olefin fractions such as ethylene, propylene, and butylene, as well as butadiene and higher conjugated diolefins. These materials are particularly valuable for the manufacture of high octane blending agents by polymerization or alkylation, or for by-product manufacture. The toluene-containing fraction withdrawn from fractionating tower 28 through line 34 was cooled with water in cooler 36 thence discharged through line 38 into a refrigeration zone 40 where it was cooled to a temperature in the neighborhood say of -40° F. The refrigeration may be effected by liquid propane or any other known or convenient

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method. The refrigerated fraction was then withdrawn from zone 40 through line 42 and discharged into a solvent treating tower 46 at a point near the bottom thereof, as indicated. At the same time, chilled liquid SO₂ was discharged into solvent treating tower 46 through line 50 at a point near the top thereof. In the tower the hydrocarbon oil passes upwardly against the downwardly flowing SO₂, thus forming a raffinate and an extract fraction. The raffinate portion, which is enriched in paraffinic constituents and also containing some SO₂, was withdrawn from tower 46 through line 52 into stripper 53 in which the SO₂ is removed through line 55 and the SO₂-free raffinate through line 54. The SO₂ from the raffinate thence passes through line 55 to SO₂ storage drum 80 from which point it was recycled through line 56 and pump 57 by means of line 50 to the extraction tower 46.

The extract fraction, on the other hand, was withdrawn through line 65 and then discharged into a washing tower 67 at a point near the top thereof. At the same time, isopentane was discharged into tower 67 through line 68 near the bottom thereof. The effect of the isopentane is to displace the non-aromatic hydrocarbons contained in the SO₂ extract and substitute isopentane so that the extract at the bottom of the tower will contain SO₂, aromatic hydrocarbons, and substantially no non-aromatic hydrocarbons except isopentane. This result is accomplished by a sort of mass action effect wherein the large preponderance of isopentane over the non-benzenoid hydrocarbons in the extract causes substantially the complete removal of the latter from the extract. The advantage of replacing the hydrocarbons originally in the extract with isopentane is that the aromatics and isopentane may eventually be separated from each other by simple distillation due to the fact that there is a rather wide hiatus in the boiling points between the two substances. The non-benzenoid hydrocarbons originally in the SO₂ extract had a boiling point in close proximity to that of the aromatics and therefore a separation could not be effected by simple distillation. The non-benzenoid hydrocarbons originally in the extract, together with the isopentane, are withdrawn from the top of tower 67 through line 70, from which they may be delivered through coil 71 disposed in furnace setting 83 and thence through line 72 into tower 121 in which isopentane is separated from the higher boiling non-benzenoid hydrocarbons, the isopentane being returned through line 125 to cooler 73 thence to storage drum 76 through line 74. Isopentane for tower 67 is supplied from storage drum 76 through line 77 and pump 81 thence to line 68. The SO₂ extract is withdrawn from the bottom of the tower through line 75, delivered to stripper 78 in which the SO₂ may be separated from the aromatics, compressed, refrigerated and return through line 79 to storage drum 80 and returned through line 56, pump 57 and thence line 50 to tower 46. The aromatic compounds are withdrawn from the solvent recovery system through line 82 and thence intimately mixed with an acid, such as sulfuric acid, introduced through line 92 at point 93, this mixture being discharged into separating drum 90 through line 91. Acid sludge is withdrawn from separating drum 90 through line 94 and the acid treated oil through line 96 into tower 98. A dilute solution of some alkali such as sodium hydroxide in water was discharged into tower 98 through line 100 and passes downward-

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ly against the upwardly flowing aromatics, thus neutralizing and washing any acid associated with the said aromatics. The washing medium was withdrawn from tower 98 through line 102. This acid treating step was necessary to remove the very small quantity of olefins present in the aromatic extract, these olefins being objectionable in nitration grade toluene. The purified aromatics and isopentane mixture was withdrawn from wash tower 98 through line 106 and delivered to a heating coil 84 where the hydrocarbons are heated to vaporization temperature, thence discharged through line 112 into a fractionating column 114. Mixed xylenes and a small quantity of toluene are withdrawn from the bottom of fractionating column 114 through line 113, the major portion of the toluene passing overhead as vapor through line 115 into the fractionating tower 117. Purified toluene of better than 99 per cent purity was withdrawn from tower 117 through line 116 thence discharged into a cooler 118 and finally through line 120 into a receiving drum 128. Overhead vapors from fractionating column 117 consisting of isopentane, benzene, and a small quantity of toluene pass overhead through line 119 in which they are combined with the isopentane fraction from extraction tower 67. The combined stream is fractionated in column 121 into isopentane as an overhead fraction for return to the extraction system and a bottoms fraction consisting of small quantities of benzene, toluene and non-benzenoid hydrocarbons. This bottoms fraction is withdrawn from fractionating column 121 through line 122 and combined with the mixed xylene fraction from tower 114, the mixture being transferred through line 123, pump 124 and line 126 to the fractionating system following the cracking operation for recovery of the small quantities of toluene which escaped the extraction or distillation zones in the first-pass through the equipment.

In the preceding description, all of the equipment necessary to effect the separation of isopentane and/or SO₂ from the products has not been illustrated because these means are well known to those skilled in the solvent extraction art. Likewise, the method of refrigerating the SO₂ and the hydrocarbons has not been described in detail because various methods are known in the art for accomplishing these results.

In the preceding example, we have set forth a preferred modification of our invention, but it is to be distinctly understood that our invention is not limited to these precise details. For example in the cracking coil 3, we may use the following range of conditions:

Pressure..... Subatmospheric to 125 lbs.
 Temperature..... 1100° F.-1400° F.
 Time of residence in
 coil, in seconds..... 0.5-15.0

Although steam is not absolutely necessary in the above described cracking operation, we have found that the use of steam or any other gaseous medium is desirable as it permits the production of a greater quantity of aromatics under otherwise constant operating conditions. Also, the use of steam appears preferable to gaseous fractions in that it can easily be condensed and removed from the system.

Furthermore, with respect to the washing medium or diluent employed in tower 67, the same need not be isopentane but may be any non-aromatic hydrocarbon which has a different boiling point from the aromatics contained in said ex-

tract. Instead of using SO_2 , we may use any solvent which has a greater solvent action for aromatic hydrocarbons than for non-aromatic hydrocarbons. As to the charging stock, it is pointed out that for best results the same should be substantially free of olefins.

Furthermore, this invention is not limited to the production of substantially pure toluene, as benzene of equal purity can be produced by charging a fraction boiling from approximately 150°F . to 200°F . to the extraction step. Also, mixed xylenes containing ortho-, meta-, and para-xylene and ethyl benzene can be produced in high purity by charging a fraction boiling from approximately 260°F . to 310°F . to the extraction step.

To recapitulate, our invention comprises cracking a petroleum oil thermally at high temperatures and during a short residence time in the cracking coil, fractionating and recovering a cut boiling within the range of the desired aromatic, subjecting this latter fraction to solvent extraction with a material such as SO_2 having a preferential solvent action for aromatics, removing the SO_2 extract to a washing tower where it is contracted with a non-benzenoid hydrocarbon having a different boiling point than the desired aromatic so as to form a second extract consisting essentially of SO_2 , or the like, the desired aromatic and the washing agent separating the SO_2 or other aromatic solvent from the hydrocarbons, and finally distilling the hydrocarbons to recover the desired aromatic.

What we claim is:

1. A method of producing nitration grade toluene of over 99% purity from paraffinic petroleum gas oil hydrocarbons which comprises heating paraffinic petroleum gas oil hydrocarbons of about 500°F . to 700°F . boiling range in the presence of a large amount of steam to a temperature of about 1200°F . to 1400°F . for a period of about $\frac{1}{2}$ to 15 seconds at a pressure of not more than 150 lbs./sq. in., fractionating the reaction products, recovering a fraction boiling within the range of from about 200°F . to 250°F ., condensing said fraction, cooling said condensed fraction in a refrigeration zone, treating said cooled fraction with liquid sulfur dioxide to form an extract, washing said extract with isopentane, separating sulfur dioxide from said extract, treating said extract with acid to remove olefins, neutralizing the acid-treated extract and fractionating the extract to recover nitration grade toluene.

2. A method of producing nitration grade toluene of over 99% purity from paraffinic petroleum gas oil hydrocarbons boiling within the range of from about 500°F . to about 700°F . which comprises heating the hydrocarbons in the presence of about 80 mol % of steam to a temperature of about 1200°F . for a period of about 2.7 seconds at a pressure of about 8 lbs./sq. in., fractionating the reaction products, recovering a fraction boil-

ing within the range of from about 200°F . to 250°F ., condensing said fraction, cooling said condensed fraction to a temperature of about -40°F ., treating said cooled fraction with liquid sulfur dioxide to form an extract, washing said extract with isopentane, separating sulfur dioxide from said extract, treating said extract with acid to remove olefins, neutralizing the acid-treated extract and fractionating the extract to recover nitration grade toluene.

3. In the process of recovering toluene from a hydrocarbon fraction boiling between about 200° and about 250°F . obtained by thermally steam-cracking paraffinic gas oil hydrocarbons boiling within the range from about 500° to 700°F . at temperatures of about 1200° to 1400°F ., contact times of about $\frac{1}{2}$ to 15 seconds and pressures not higher than 150 lbs./sq. in., the steps comprising condensing said fraction, cooling said condensed fraction in a refrigeration zone, treating said cooled fraction with liquid sulfur dioxide to form an extract, washing said extract with isopentane, separating sulfur dioxide from said extract, treating said extract with acid to remove olefins, neutralizing the acid-treated extract and fractionating the extract to recover nitration grade toluene.

4. The method set forth in claim 3 wherein said condensed fraction is cooled to a temperature of about -40°F .

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