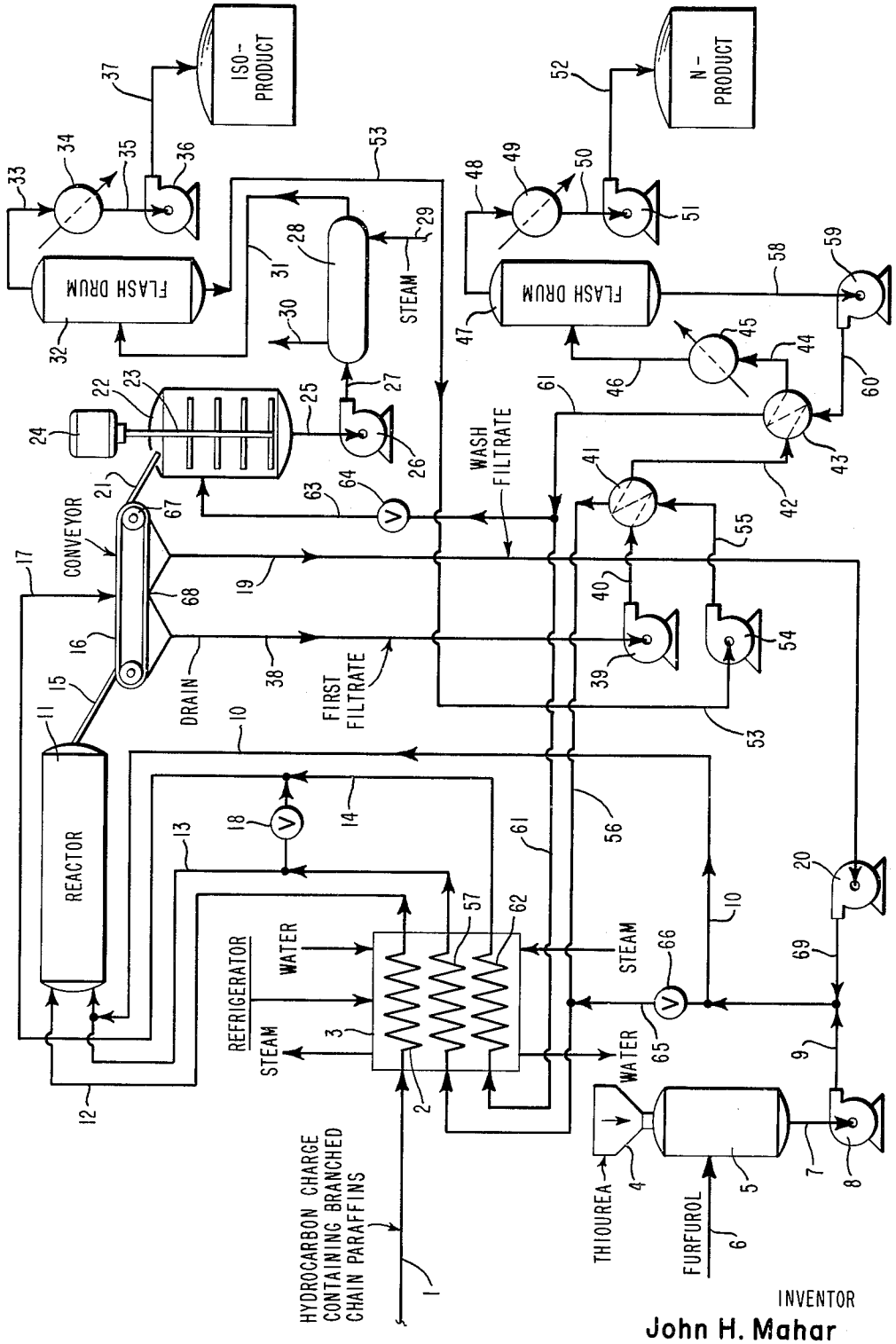
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THIOUREA ADDUCTION

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THIOUREA ADDUCTION

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The present invention relates to the separation of branched chain paraffins from mixtures comprising normal and isoparaffins employing thiourea as the adducting material and furfuryl alcohol (furfurol) as the solvent and/or promoter and, more particularly, to the upgrading of gasoline and of jet fuels through thiourea adduction employing furfuryl alcohol as the solvent and/or promoter.

The separation of branched chain paraffins or isoparaffins from mixtures comprising normal and branched chain paraffins by adduction of the isoparaffins with thiourea employing as promoters and/or solvents the lower aliphatic alcohols, i.e., aliphatic alcohols having not more than four carbon atoms and preferably methanol, has been described in several technical publications and United States Patents. However, the separation of the promoter-solvent from the raffinate and from the adduct when using the C_1 to C_4 alcohols requires sophisticated fractionating equipment. This can be readily understood when the boiling points of the C_4 to C_8 isoparaffins and the boiling points of the C_5 to C_8 normal paraffins are compared with the boiling points of the C_1 to C_4 aliphatic alcohols. This comparison is made in Table I.

TABLE I

C_5 to C_8 normal paraffin, B.P., ° F.	C_1 to C_4 alkanol, B.P., ° F.	C_5 to C_8 isoparaffin, B.P., ° F.
C_5—96.9		C_5—82.2
		C_5—49.0
	C_1—148.1	C_6—140.5
C_6—155.7		C_6—145.9
		C_6—121.5
		C_6—136.4
C_7—209.2		C_7—194.1
	C_2—173.0	C_7—197.5
	n—C_3—207.0	C_7—200.2
	i—C_3—180.2	C_7—174.6
		C_7—193.6
	n—C_4—243.9	C_7—176.9
	sec—C_4—211.1	C_7—186.9
	i—C_4—226.4	C_7—100.2
C_8—258.2	t—C_4—180.7	C_8—114.2

However, a simple separation means such as a flash drum would reduce capital costs, maintenance costs, and operating costs. Such a simple fractionation means as a flash drum is only efficient enough when the boiling points of the materials to be separated differ by at least 100 degrees Fahrenheit. Not only must the difference between the boiling point of the promoter-solvent and the boiling point of the adducted hydrocarbon and the non-adducted hydrocarbon be at least 100 degrees Fahrenheit but the promoter-solvent must also have the capabilities of the lower aliphatic alcohols to enhance the information of the thiourea-hydrocarbon adduct and be a solvent for thiourea miscible with hydrocarbon mixtures to be resolved. It has now been discovered that furfuryl alcohol often referred to as furfurol has the desired characteristics of a promoter-solvent and the boiling point which requires only a simple fractionator such as a flash drum or splitter for separation of the adducted hydrocarbon from the thiourea and for separation of the non-adducted hydrocarbon from the promoter-solvent. This becomes manifest from a consideration of the boiling

point of furfurol and the boiling range of the product of the isomerization of the C_5–C_6 fraction of straight run naphtha. The C_5–C_6 fraction of straight run naphtha has a boiling range of 80° to 170° F. The isomate boils within approximately the same range. On the other hand, furfuryl alcohol or furfurol boils at 338° F. Thus a very simple means for fractionating the mixture of non-adducted hydrocarbons and promoter-solvent and for fractionating the decomposed thiourea adduct suffices when furfuryl alcohol is employed as the promoter-solvent. Furfurol possesses the characteristics of a promoter-solvent for thiourea adduction as is manifest from the data presented in Table II.

TABLE II (TV–12)

Isomate—Aluminum chloride isomerization product	
Octane number (Research—3 cc. TEL)	94.2
Mol ratio thiourea:furfurol:isomate=5.7:5.0:1.0.	
Adducting temperature, ° F.	80–90
Washing temperature, ° F.	80–90
Hydrocarbon from:	Octane number (Research+3 cc. TEL)
First filtrate	90.2
Stripped from particle-form solid adduct	102.6

It will be observed that the octane number of the hydrocarbons separated from the thiourea adduct was 8.5 octane units higher than that of the isomate. Therefore, there can be no question that furfurol is a promoter in the adduction of isoparaffins with thiourea.

Illustrative of the upgrading of isomate are the following examples.

Example I

A mixture of equal parts of isomate and C_5 to 170° F. fraction of straight run naphtha (said isomate being the product of the isomerization of n-hexane using aluminum chloride as a catalyst) to provide 2,432.6 parts by weight of said mixture, i.e., 519.6 parts by weight (6.6 mols) of hydrocarbon, 1,113 parts by weight of furfuryl alcohol (11.3 mols) and 800 parts by weight of thiourea (10.5 mols) were mixed and held at an adduct formation temperature of about 84° F. for one hour. The mixture was filtered to yield a first filtrate of 1,093 parts by weight. The adduct crystals were washed twice with fresh furfuryl alcohol totaling 1,455 parts by weight (about 15 mols).

The washed particle-form solid adduct was mixed with 1,114 parts by weight (about 11.3 mols) of fresh furfuryl alcohol. The mixture of washed particle-form solid adduct and furfuryl alcohol was heated to a maximum still temperature of 300° F. and a maximum overhead temperature of 138° F. The hydrocarbons recovered from the washed particle-form solid adduct was 108.1 parts by weight. The first filtrate was heated to a maximum overhead temperature of 196 degrees F. and 293.6 parts by weight of hydrocarbons recovered. The wash filtrate was heated to a maximum overhead temperature of 205 degrees F. and 65.5 parts by weight of hydrocarbons recovered.

The mixture of isomate and naphtha had an octane rating R+3 cc. TEL) of 91.6. The hydrocarbon recovered from the adduct had an octane rating of (R+3 cc. TEL) of 101.0. In other words, the mixture of isomate and C_5 to 170 degrees F. straight run naphtha was upgraded about 10 octane numbers. The hydrocarbon from the first filtrate had an octane rating of 86.5 (R+3 cc. TEL). Thus it is manifest the furfuryl alcohol, sometimes designated furfurol is very effective in the thiourea-adduct separation of isoparaffins from n-paraffins.

The charge mixture, the hydrocarbons from the adduct, and the hydrocarbons from the first filtrate were analyzed

by the Mass Spectograph method with the following results:

TABLE III

Component	Charge Mixture, weight (percent)	Hydrocarbons from adduct, weight (percent)	Hydrocarbons from first filtrate, weight (percent)
i-Butane	0.34	0.25	0.34
i-Pentane	6.40	6.07	7.31
2,2-dimethylbutane	10.61	31.46	----
2,3-dimethylbutane	5.09	10.33	2.78
2-methyl pentane	24.46	10.29	31.22
3-methyl pentane	12.48	6.56	15.53
Total	49.38	64.96	57.18
n-Butane	1.59	0.60	1.86
n-Pentane	10.59	3.14	12.27
n-Hexane	16.57	4.40	22.19
Heptanes	1.73	1.08	1.18
Total	30.48	9.22	37.50
Cyclopentane	1.37	2.98	0.09
Cyclohexane	1.81	8.31	0.18
Methylcyclopentane	6.03	13.58	3.85
Total	9.21	24.87	4.12
Benzene	0.85	0.94	0.62
Pentenes	0.10	----	0.40

The same products as well as the hydrocarbons recovered from the wash filtrate were analyzed by "Gas Partition Chromatography" with the results set forth in Table IV.

TABLE IV

Component	Charge Mixture, weight (percent)	Hydrocarbons from adduct, weight (percent)	Hydrocarbons from first filtrate, weight (percent)	Hydrocarbons from wash filtrate weight (percent)
i-Butane	0.74	0.60	0.44	0.39
i-Pentane	3.83	8.85	7.18	7.63
2,2-dimethylbutane	12.74	34.59	6.65	12.33
2,3-dimethylbutane	5.85	9.47	3.38	4.87
2-methyl pentane	21.72	11.67	24.85	18.73
3-methyl pentane	12.74	7.11	12.50	12.86
Total	57.62	72.29	55.00	56.81
n-Butane	2.00	1.07	2.28	1.49
n-Pentane	11.93	5.15	13.93	12.57
n-Hexane	16.79	4.81	23.00	18.23
Heptanes	0.51	0.05	0.69	0.20
Total	31.23	11.08	39.90	32.49
Cyclopentane	3.09	3.00	1.31	1.96
Cyclohexane	2.83	5.18	0.28	2.25
Methylcylcopentane	5.09	8.44	3.35	6.28
Total	11.01	16.62	4.94	10.49
Pentenes	----	----	0.10	0.10

From the foregoing analyzes and from the octane ratings set forth hereinbefore it is manifest that the components of the charge mixture having the higher octane ratings, i.e., the branched chain paraffins and the cyclic hydrocarbons enriched the hydrocarbons recovered from the adduct.

Example II (TV # 14)

Thiourea, furfuryl alcohol, and adductable hydrocarbons were mixed in the mol ratio of 4:4:1 and agitated for about one hour at ambient temperature (80° to 90° F.). The products and the octane ratings (Research +3 cc. TEL) thereof are set forth in Table V.

TABLE V

Product:	Octane Rating (R+3 cc. TEL)
Charge Mixture	91.6
Adducted Hydrocarbons	97.7
Hydrocarbons from First Filtrate	89.3
Hydrocarbons from Wash Filtrate	91.5

Those skilled in the art will recognize that separation of branched chain paraffins by adduction with thiourea in the presence of furfuryl alchol can be used to separate normal paraffins having at least four carbon atoms from branched chain paraffins having four or more carbon atoms in the chain. Thus, a middle distillate, for example kerosine comprising normal paraffins, isoparaffins, cycloparaffins and aromatics having a luminometer number of about 70 can be converted into jet fuel having a luminometer rating of at least 100 by reforming the kerosine in the presence of a reforming catalyst comprising platinum group metal on alumina support to convert substantially all of the cycloparaffins to aromatics. The C_8 and heavier reformate is contacted with molecular sieve material having pores of about 4 to 5 Angstroms diameter to produce a sieve effluent comprising isoparaffins, and cyclic hydrocarbons and a sorbate comprising normal paraffins. The effluent is treated with thiourea and furfuryl alcohol to the form a thiourea adduct, comprising the isoparaffin and thiourea. The adduct is washed with furfuryl alcohol. The washed adduct is then decomposed to yield isoparaffins and thiourea dissolved in furfuryl alcohol. The separated isoparaffins are blended with the n-paraffin sieve sorbate to provide an improved jet fuel having a luminometer number of at least 100 and a lower pour point than the unblended sieve sorbate n-paraffins.

Alternatively, the sieve effluent can be extracted with a selective solvent such as sulfur dioxide, di-chlorodiethyl ether and the like having a greater affinity for more aromatic hydrocarbons than for more paraffinic hydrocarbons to obtain an aromatic extract comprising selective solvent and aromatic hydrocarbons and a raffinate comprising iso-paraffins and solvent. The isoparaffins are separated by distillation from solvent and the separated isoparaffins blended with the sieve sorbate n-paraffins to provide a blended jet fuel having a luminometer number of at least 100 and a lower pour point than the unblended sieve sorbate. The aromatic hydrocarbons are recovered in either alternative method of separation for conversion to aromatic hydrocarbons boiling in the gasoline range (dealkylation) or for use per se as aromatic hydrocarbons.

Illustrative of the present method of separating isoparaffins from n-paraffins is the flow of liquids and adduct slurry provided by the flow sheet of the drawing. The flow sheet of the drawing illustrates the separation of the high octane components from the low octane components of an isomate produced by the isomerization of n-paraffins in the presence of aluminum chloride. It will be observed that only a flash drum is required to fractionate or separate the promoter-solvent from the non-adducted hydrocarbons and that the adduct can be decomposed and the adducted hydrocarbons separated from the thiourea dissolved or suspended in furfurol in a very simple fractionating apparatus, to wit: a flash drum or equivalent.

The maximum temperature for adduction and adduct washing is in general, the maximum temperature of the adductable hydrocarbons, i.e., isoparaffins. The minimum temperature for adduction and adduct washing is the freezing point of furfuryl alcohol, i.e., plus 5° F. The prefered temperature for adduct formation and washing of the adduct particles to separate the higher octane components from the lower octane components of a mixture of hydrocarbons boiling in the gasoline range, i.e., isomate, naphtha reformate, naphtha raffinate and the like is in the range of about 40° to about 100° F.

In accordance with the principles of the present invention a solution of thiourea in furfuryl alcohol or a slurry of crystals of thiourea in furfuryl alcohol or a supersaturated solution of thiourea in furfuryl alcohol is prepared in tank **5** in any suitable manner. Thus, thiourea particles are introduced into tank **5** in any suitable manner as by means of hopper **4**. Furfuryl alcohol is pumped by a pump (not shown) from a source (not shown) through pipe **6** into tank **5**. The particles of

thiourea dissolve at least in part in the furfuryl alcohol to provide a solution of thiourea or a slurry of thiourea in furfuryl alcohol in tank **5**. Preferably the temperature in tank **5** is in the range of about 50° F. to about 150° F. The solution or slurry of thiourea in furfuryl alcohol flows from tank **5** through pipe **7** to the suction side of pump **8**. A start-up the thiourea solution or slurry is pumped by pump **8** through pipes **9** and **65** under control of valve **66** to pipe **56** and thence to coil **57** in means for cooling **3**. Presently preferred for cooling the reactant is the well known steam jet refrigerator. After start-up valve **66** is closed and a make-up quantity of thiourea furfuryl solution or slurry is pumped by pump **8** through pipes **9** and **10** to pipe **13**.

In cooler or refrigerator **3** the reactant i.e., charge stock hydrocarbon mixture comprising iso-paraffins and n-paraffins, e.g., isomate or isomate and C_5 to 170 degrees F. fraction of straight run gasoline is cooled to a temperature at which thiourea forms an adduct with iso-paraffins. Thus, for example, the reactants are cooled to at least 100 degrees F., preferably to a temperature in the range of about 40 degrees to about 100 degrees F., or even as low as about 6 degrees to about 10 degrees F.

The charge stock comprising isoparaffins and normal paraffins or molecular sieve effluent, or selective solvent raffinate, e.g., a mixture of isomate (C_6) and C_5 to 170 degrees F. naphtha flows from a source not shown through pipe **1** to coil **2** in cooler or refrigerator **3**.

After start-up, first filtrate, obtained as hereinafter described, flowing from pump **59** through pipe **61** to coil **62** comprising furfuryl alcohol and traces of charge stock is cooled in coil **62** to the adduct formation temperature.

After start-up raffinate residue (obtained as described hereinafter) comprising furfuryl alcohol, thiourea, and traces of isoparaffins flows from pump **54** through pipes **55** and **56** to coil **57**. In coil **57** the raffinate residue is cooled to adduct formation temperature.

The charge stock to adduct formation temperature, i.e., maximum temperature below the boiling point of highest boiling adductable hydrocarbon, preferably not higher than about 100 degrees F., minimum temperature about 6 degrees to about 10 degrees F., preferred minimum temperature about 40 degrees F., flows from coil **2** through pipe **12** to reactor **11**. The first filtrate cooled to adduct formation temperature in coil **62** flows therefrom through pipe **14** to pipe **17** for use as wash liquid. Raffinate residue cooled in coil **57** to adduct formation temperature flows through pipe **13** in part to reactor **11** and in part through pipe **17** under control of valve **18** to conveyor **16** for use as wash liquid in washing the adduct particles to remove adhering charge stock as completely as practicable.

It is to be noted that the flow of reactants through coils in cooler or refrigerator **3** is controlled so that while the temperature of each reactant, i.e., charge stock, first filtrate and raffinate residue, is in the range of adduct formature temperature the temperatures of the reactants can be different. The controlling temperature is the temperature of the mixture of charge hydrocarbons, furfuryl alcohol and thiourea in reactor **11**. The temperature in reactor **11** is an adduct formation temperature less than the boiling point of the highest boiling adductable hydrocarbon, preferably not higher than 100 degrees F., and not below about 6 degrees F.

The charge mixture, the first filtrate, the raffinate residue and the make-up furfuryl alcohol-thiourea solution or slurry and wash filtrate flowing respectively from pumps **8** and **20** through pipe **10** to pipe **13** enter reactor **11** in proportion to provide a thiourea to furfuryl alcohol to charge mixture mol ratio in the range of 1:1:1 to 25:25:1 preferably in the range of 3:3:1 to 15:15:1 and at a temperature in the adduct formation temperature range set forth hereinbefore.

The adductable hydrocarbons of the charge mixture, i.e., the isoparaffins form with the thiourea a particle form solid adduct at the adduct formation temperature. The reaction mixture including the particle form solid adduct flows from reactor **11** through pipe or trough or chute **15** to means for separating the particle form solid adduct from the reaction mixture. Means for separating the adduct particles from the reaction mixture include filter presses, Dorr classifiers and the illustrated conveyor comprising a membrane permeable to furfuryl alcohol and hydrocarbon mounted for movement of the adduct particles from chute or pipe **15** to apron or chute **21** whilst liquid reaction mixture drains from the adduct particles to conduit **38** and wash liquid drains through conduit **19**. Thus, the conveyor belt **16** can be flexible continuous foraminous belt moved in any suitable manner as by a motor driven drum **67**. The reaction mixture and adduct particles suspended therein flows from pipe or chute **15** onto a belt **16**. The liquid reaction mixture drains through the belt into pipe **38**. (The liquid reaction mixture which drains through the belt **16** to flow through conduit **38** is designated first filtrate hereinafter.) The first filtrate comprising furfuryl alcohol, non-adducted hydrocarbons, and non-adducted thiourea flows through conduit **38** to the suction side of pump **39**. Pump **39** discharges the first filtrate into pipe **40**. The first filtrate flows through pipe **40** to indirect heat exchanger **41**. In indirect heat exchanger **41** the first filtrate is in heat transfer relation with raffinate residue flowing from flash drum **32**. From indirect heat exchanger **41** the first filtrate flows through pipe **42** to indirect heat exchanger **43**. In indirect heat exchanger **43** the heated first filtrate is in heat transfer relation with the bottoms of flash drum **47**. From indirect heat exchanger **43** the first filtrate flows through pipe **44** to indirect heat exchanger **45**. In the indirect heat exchanger **45** the first filtrate is heated in any suitable manner as by steam to a temperature at which the normal paraffins of the charge mixture are separated from furfuryl alcohol by vaporization. As illustrated the n-paraffins have lower boiling points than furfurol, i.e., the n-paraffins boil below about 180 degrees F. On the other hand, in the event that the n-paraffins boil above the boiling point of furfuryl alcohol, i.e., above 338 degrees F. the first filtrate is heated to a temperature at which furfuryl alcohol is vaporized at atmospheric or sub-atmospheric pressure.

The heated first filtrate flows from indirect heat exchanger **45** through pipe **46** to flash drum or spliter **47**. In flash drum or spliter **47** the n-paraffins of the charge mixture are taken as an overhead through pipe **48**. The n-paraffin overhead flows through conduit **48** to cooler **49**. In cooler **49** the n-paraffin overhead is cooled to a temperature at which the most volatile n-paraffins of the charge mixture is condensed. The condensed n-paraffins flow from cooler **49** through pipe **50** to the suction side of pump **51**. Pump **51** discharges the n-paraffins into pipe **52** through which the n-paraffins flow to storage, blending, distribution and the like.

Returning now to means **68** for separating adduct particles from liquid reaction mixture and wash liquid; the adduct particles on belt **16** pass the point at which the preponderant portion of the liquid reaction mixture has drained from the adduct particles to drain **38**. Thereafter the adduct particles are washed with raffinate residue flowing from coil **57** through pipes **13** and **17** under control of valve **18** at an adduct formation temperature in the range set forth hereinbefore, i.e., at a temperature not in excess of 100 degrees F. The raffinate residue, comprising thiourea from the adduct particles and furfuryl alcohol, flows from pipe **17** over the adduct particles on the foraminous continuous belt **16** and washes adhering or adduct entrained reaction mixture, primarily nonadducted hydrocarbons, from the adduct particles. The wash liquid and adduct particle washings, designated wash filtrate hereinafter, flows through conduit **19** to the suction side of pump **20**. Pump **20** discharges the wash filtrate into pipe **69**. The wash filtrate comprising

furfuryl alcohol and non-adducted hydrocarbons of the charge mixture flows through pipe **69** to pipe **10**. In pipe **10** the wash filtrate is mixed with make-up furfuryl alcohol-thiourea solution or slurry flowing from pipe **9**. The mixed wash filtrate and make-up furfuryl alcohol-thiourea solution or slurry flows through pipe **10** to pipe **13** and thence to reactor **11**.

The adduct particles deposited on belt **16** are discharged onto apron or chute **21** down which the adduct particles flow to tank **22** provided with an agitator **23** driven by electric motor **24** or any other suitable means. Tank **22** is also provided with inlet means for introducing furfuryl alcohol or bottoms from flash drum **47** into tank **22**.

The adduct particles and added furfuryl alcohol or flash drum bottoms flow from tank **22** through pipe **25** to the suction side of pump **26**. Pump **26** discharges the adduct and furfuryl alcohol into pipe **27**, through which the mixture flows to means for decomposing the adduct into adducted hydrocarbons and thiourea. (The amount of furfuryl alcohol introduced into tank **22** is at least sufficient to provide a solution of thiourea in furfuryl alcohol at the temperature in votator or decomposer **28**, i.e., at a temperature below 300 degrees F.)

In votator or decomposer **28** the mixture of adduct and furfuryl alcohol, i.e., first filtrate bottoms of flash drum or splitter **47**, is heated in any suitable manner as by an immersed steam coil into which steam flows through pipe **29** and from which steam flows through pipe **30** to a temperature above 100 degrees F. and below 300 degrees F. e.g., a temperature in the range of about 150 degrees to about 280 degrees F. at which the adduct is decomposed into adducted hydrocarbons, i.e., isoparaffins and adduct, i.e., thiourea. The mixture of furfuryl alcohol, thiourea, and isoparaffins flows from votator **28** through pipe **31** to flash drum or splitter **32**.

In flash drum or splitter **32** the adducted hydrocarbons are taken overhead through pipe **33**. The adducted hydrocarbons flow through pipe **33** to cooler **34**. In cooler **34** the adducted hydrocarbons are cooled to a temperature at which the lowest boiling adducted hydrocarbon is liquid. The cooled adducted hydrocarbons flow from the cooler **34** through pipe **35** to the suction side of pump **36**. Pump **36** discharges the adducted hydrocarbons into pipe **37** through which the adducted hydrocarbons flow to storage, blending, distribution, etc.

The bottoms of flash drum or splitter **32**, designated raffinate residue, flow therefrom through pipe **53** to the suction side of pump **54**. Pump **54** discharges the raffinate residue into pipe **55**. The raffinate residue comprising furfuryl alcohol and thiourea (from the adduct particles) flows through pipe **55** to indirect heat exchanger **41**. In heat exchanger **41** the raffinate residue is in heat transfer relation with the first filtrate. From indirect heat exchanger **41** the raffinate residue flows through pipe **56** to coil **57** in refrigerator **3**.

Illustrative of the separation of higher octane rating hydrocarbons from lower octane rating hydrocarbons of aluminum chloride isomate are the data presented in Table VI.

TABLE VI

Run No.	11	12	13	14	15	16	19
Thiourea, mols	5.9	5.7	5.7	4.0	7.0	7.0	8.8
Furfuryl Alcohol, mols	4.3	5.0	6.1	3.9	6.8	6.8	8.7
Hydrocarbon,[1] mols	1	1	1	1	1	1	1
Mixing time, hours	1.25	2.33	1.0	1.0	1.0	1.0	1.0
Adduct formation temperature, degrees F	80-90	80-90	84	80-90	80-90	80-90	80-90
Wash solvent, furfuryl alcohol: Volume of solvent each wash [2]	0.6	0.6	1.3	1.78	0.83	0.93	0.78
Number of washes	1	2	2	3	3	3	4
Adduct decomposition							
Solvent volume[2], furfuryl alcohol	1	1.4	1.25	1	1.25	1.25	2.8
Maximum solvent stripping temp. ° F	220 (B)	298 (B)	300 (B)	189 (T)	215 (T)	155 (T)	155 (T)
Recovered high octane hydrocarbons, percent by weight	37.5	34.2	23.2	6.7		24.7	39.5
Maximum octane No. increase	5.5	8.4	9.4	5.2		6.6	4.6

[1] C_6 isomate ($AlCl_3$ Catalyst).
[2] Based on hydrocarbon charge.
B—Still. T—Overhead.

A tabulation of the total volume of furfuryl alcohol used to wash the adduct particles, the weight percent yield of high octane components recovered, and the increase in octane rating provides interesting information.

TABLE VII

Run No.	Total volume of wash	Weight percent recovered	Δ Octane No.	100 (R×Δ)	Vol. hydrocarbons
11	300	37.5	5.5	206	300
12	600	34.2	8.4	287	500
13	1,300	23.2	9.4	218	800
14	2,670	6.7	5.2	36	800
15	1,240				800
16	1,400	24.7	6.6	163	800
19	1,550	39.5	4.6	182	355

From the foregoing tabulations, Table VI and VII, it is manifest that the total volume of wash liquid, i.e., furfuryl alcohol, based upon the volume of charge hydrocarbons preferably is in the range of 0.6 to 1.6.

I claim:

1. A method of separating branched chain paraffins from straight chain paraffins which comprises mixing (1) a charge hydrocarbon mixture comprising branched chain paraffins and straight chain paraffins, (2) thiourea, and (3) furfuryl alcohol to provide a molal ratio of thiourea: furfuryl alcohol: charge hydrocarbon mixture in the range of 1:1:1 to 25:25:1, holding the mixture so formed at an adduct formation temperature not exceeding the boiling point of the lowest boiling component of said hydrocarbon mixture and above the freezing point of furfuryl alcohol to produce a particle-form solid adduct comprising thiourea and branched chain paraffins, separating said particle-form solid adduct from liquid reaction mixture, washing said particle-form solid adduct with wash liquid comprising furfuryl alcohol to obtain washed particle-form solid adduct having a reduced content of non-adducted hydrocarbons, admixing furfuryl alcohol with said washed particle-form solid adduct to obtain a mixture for decomposing said adduct consisting essentially of particle-form solid adduct and furfuryl alcohol, heating said mixture of said particle-form solid adduct and said furfuryl alcohol at a temperature below about 300° F. to decompose said particle-form solid adduct and to produce a mixture comprising

furfuryl alcohol branched chain paraffins per se and thiourea per se, separating branched chain paraffins from said mixture at a temperature below about 300° F. and above an adduct formation temperature, and recovering said branched chain paraffins.

2. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1, wherein the charge hydrocarbon mixture comprises an isomate of C_6 hydrocarbons.

3. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein the charge hydrocarbon mixture comprises a reformate.

4. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein the charge hydrocarbons mixture comprises the effluent produced when contacting the reformate of a fuel fraction of petroleum boiling above 200° F. with molecular sieve material having 4 to 5 angstrom diameter pores.

5. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein the adduct formation temperature is below 100° F.

6. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein the molal ratio of thiourea: furfuryl alcohol: charge hydrocarbon mixture is in the range of 3:3:1 to 15:15:1.

7. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein the charge hydrocarbon mixture comprises the isomate of C_5 and C_6 paraffins and wherein the adduct formation temperature is in the range of about 40° to about 100° F.

8. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein normal paraffins are separated from the liquid reaction mixture.

9. The method of separating branched chain paraffins from straight chain paraffins as set forth in claim 1 wherein normal paraffins are separated from the liquid reaction mixture to provide normal product and first filtrate comprising furfuryl alcohol and thiourea, and wherein (1) furfuryl alcohol and thiourea obtained in the decomposition of particle-form solid adduct, designated raffinate residue, (2) the washings from washing the particle-form adduct at least in part, and (3) the aforesaid first filtrate are recycled to the adduct formation stage.

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