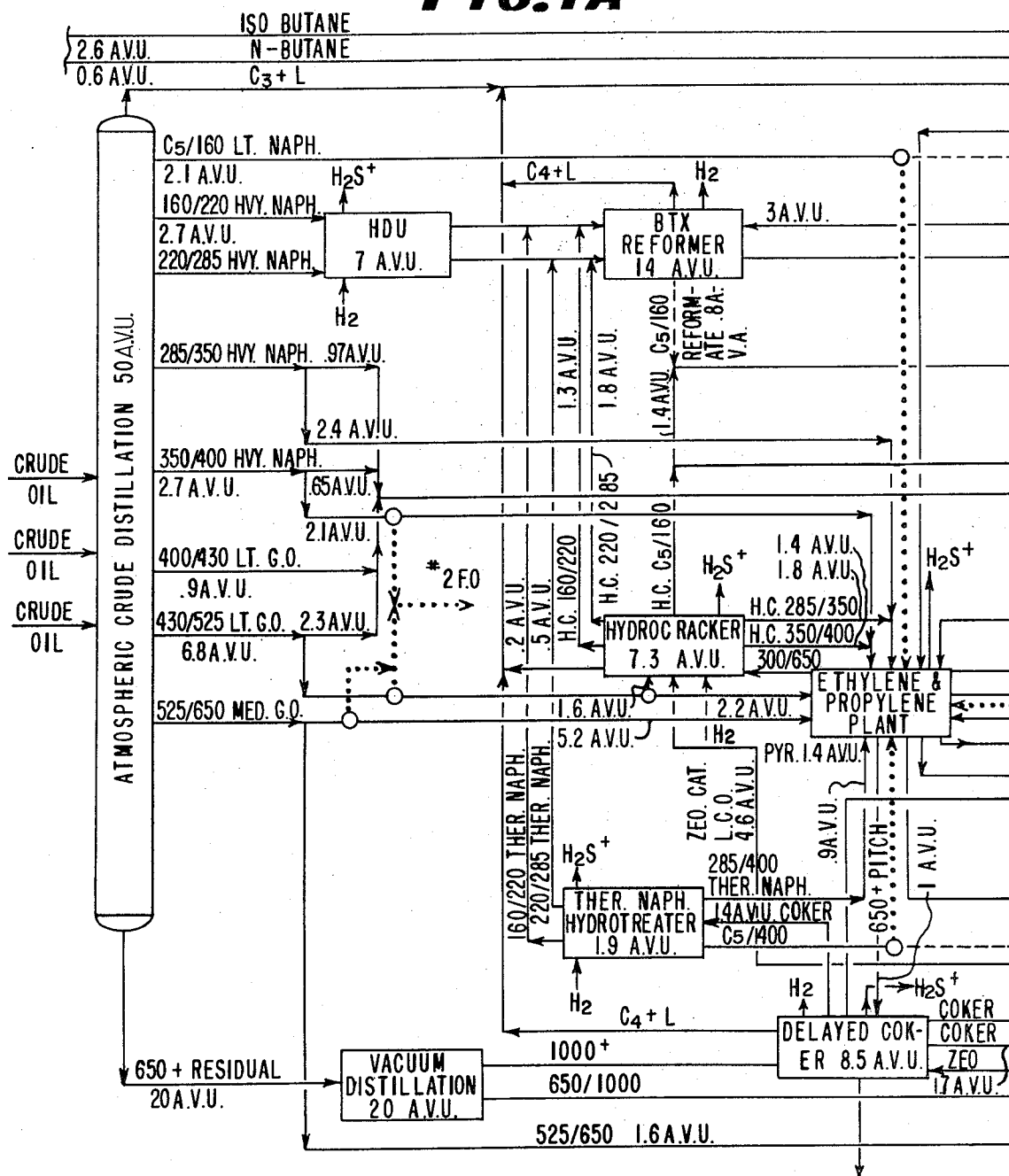


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2 Sheets-Sheet 1

FIG. 1A



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Nov. 7, 1972

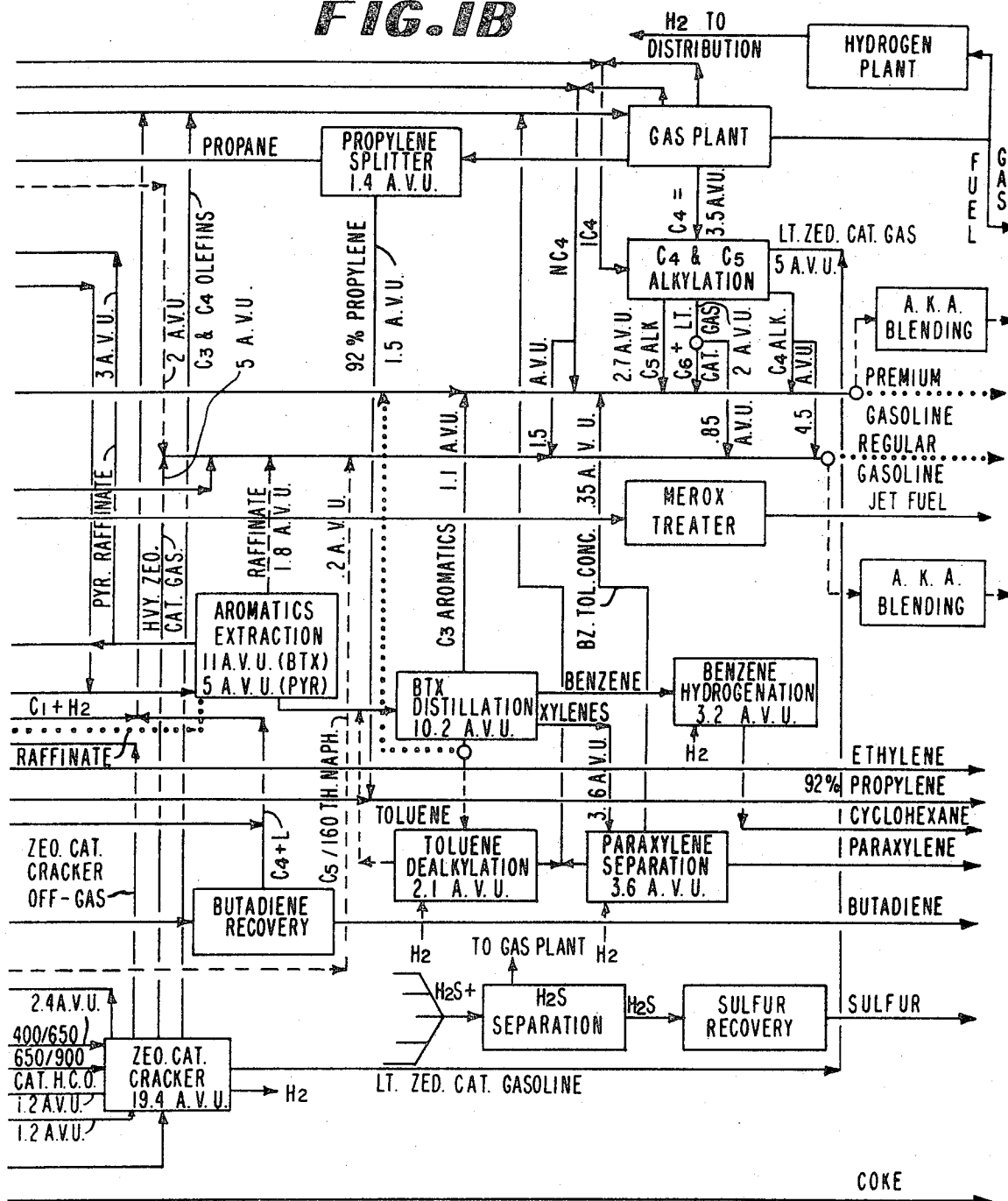
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COMPOSITE HYDROCARBON REFINERY APPARATUS AND
PROCESS ARRANGEMENT

3,702,292

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2 Sheets-Sheet 2

FIG. 1B



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3,702,292 COMPOSITE HYDROCARBON REFINERY APPARATUS AND PROCESS ARRANGEMENT

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U.S. Cl. 208—80

24 Claims

ABSTRACT OF THE DISCLOSURE

A highly integrated crude oil refinery arrangement for producing fuel and chemical products, involving crude oil distillation means, hydrocracking means, delayed coking means, reforming means, ethylene and propylene producing means comprising a pyrolysis steam cracking unit and a pyrolysis products separation unit, catalytic cracking means, aromatic product recovery means, butadiene recovery means and alkylation means in a highly flexible, closely controlled and inter-related system to produce a high conversion of crude oil to chemicals of as high as about 50% and a conversion of crude oil to gasoline and jet fuel as low as about 50% for a maximum value combination of widely varied products.

FIELD OF THE INVENTION

This invention generally relates to the field of petroleum refining and processing. More specifically the invention involves extensive, integrated, and flexible arrangements of cooperating apparatus units and process steps to separate a crude oil into a given number of fractions which are processed and interrelated in a particularly advantageous and unusual manner to produce a very high percentage of maximum value chemical products such as ethylene, propylene, butadiene, cyclohexane, para-xylene, as well as a relatively low percentage of gasoline, jet fuel, and coke.

It is an object of the invention to provide such an improved refining arrangement which is efficient, flexible, and controllable in operation yet is of a logical straight-forward design for maximum economy in construction, maintenance, and repair.

It is another object to provide such an improved refinery arrangement which is sufficiently flexible to handle widely varying feedstocks, vary the amounts and types of products made from a given feedstock, and which in addition can be converted from production of products comprising gasolines suitable for use with organo-lead antiknock additives to production of products comprising gasolines of high antiknock properties without the organo-lead additives without changing the basic component units.

Other objects and advantages will appear hereinafter.

PRIOR ART BACKGROUND OF THE INVENTION

Integrated refinery arrangements for the general production of chemical products and fuel products are known in the art. Examples of these are described in U.S. Pat. 3,409,540 and U.S. Pats. 3,060,116. The refinery arrangements shown in these patents reflect and embody the major interest of the petroleum industry in the production of gasolines, and other fuel products, of reasonably high value, with a relatively much lesser interest in the production of valuable chemical products in place of lower value fuel products. In line with this, the particular refining arrangements shown in these U.S. patents, which are believed to represent the prior art closest to the present invention, were selected, arranged, and built-up of specific component units to achieve this major objective of maximum gasoline and fuel products, with the chemical products being only of secondary or more incidental interest.

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On the other hand, the refinery arrangement embodying principles of this invention in terms of its particular component units and its process steps, and the particular arrangements and interrelationships thereof, is directed toward the achievement of the quite different results and objectives of the chemical industry which involve production of optimum amounts of chemical products which minimizing production of fuel products, such as gasolines, and jet fuels, produced and also substantially eliminating production of the lowest value fuel products.

The significantly different objectives have required significantly different refinery arrangements to achieve them.

It will become apparent from a consideration of the following detailed description and discussions of the preferred refinery arrangements of this invention, that novel and unusual features exist (1) in the particular selection of known component units or process steps, (2) in the overall flexible combination of such units or steps, and (3) in the special interactions and special relationships among the important units or steps. All of these features contribute and cooperate in a useful way not shown or suggested by the prior art to produce beneficial and desirable results not recognized by the prior art and yet of special significance to those operating in the chemical field or in the predominantly chemical side of the petrochemicals field.

The degree of flexibility in handling varying feedstocks, in varying the products and product percentages made from a given feedstock, and in producing either leaded or unleaded gasolines without changing the component units is considered to be a significant novel contribution and advance over the prior art.

SUMMARY OF THE INVENTION

Generally stated, the objects of the invention and a wide range of maximum value outputs comprising optimal production of high value chemical products such as olefins and aromatics with correspondingly lower production of higher value fuel products such as gasolines and jet fuel, are satisfactorily achieved in the improved refining process and means arrangement of this invention. In one preferred form this arrangement involves means and process steps to continuously separate by distillation a crude oil into a number of fractions, catalytically cracking a gas oil fraction from the distillation separation step to form propane, a C₂ and lower gas fraction, gas oil, and gasoline, thermally cracking a heavy residual fraction from the distillation separation step to form coke and a naphtha fraction, steam cracking (1) a gas oil fraction from the distillation separation step, (2) naphtha from said thermal cracking step, and (3) propane from the catalytic cracking step to form a heavy gas oil, tar fractions, ethylene, propylene, aromatic products, and butadiene, catalytically hydrocracking (1) a heavy gas oil from the steam cracking step, (2) a gas oil from the catalytic cracking step and (3) a gas oil from the distillation separation step to form and supply gas oil and naphtha as inputs to the steam cracking step, and further supplying the heavy gas oil and residual tar fraction from the steam cracking step as inputs to the thermal cracking step.

DESCRIPTION OF THE DRAWINGS

FIG. 1 comprised of 1A and 1A shows, an overall schematic diagrammatic showing of the system, component units, and flows of a preferred refinery arrangement embodying principles of this invention.

The refinery arrangement of FIG. 1 comprises a cooperating interrelated apparatus and component units of known conventional commercial design, constructed, interconnected, and arranged as shown for suitable conven-

tional instrumentation and control from the usual central control rooms in known manner.

The design, operation and cooperation of the cooperating apparatus and process units will be described in detail in the following sequence:

- (1) Crude Distillation
- (2) Vacuum Distillation
- (3) Delayed Coking
- (4) Thermal Naphtha Hydrotreater
- (5) Catalytic Cracking
- (6) Hydrocracking
- (7) Light Hydrocarbons Separation (Gas Plant)
- (8) C₄ and C₅ Alkylation
- (9) Straight-Run Naphtha Hydrotreater
- (10) Catalytic Reforming
- (11) Aromatics Extraction
- (12) Pyrolysis-Steam Cracking (Ethylene and Propylene producing plant)
- (13) Ethylene Purification (Pyrolysis products separation unit of Ethylene and Propylene producing plant)
- (14) Butadiene Recovery
- (15) Pyrolysis Naphtha Hydrotreater
- (16) BTX (Benzene, Toluene, Xylene) Distillation
- (17) Toluene Dealkylation
- (18) Benzene Hydrogenation
- (19) Para Xylene Separation (Isomerization and Recovery)
- (20) Hydrogen Generation
- (21) Sulfur Recovery
- (22) Merox Treatment

(1) Crude Distillation

Crude distillation separates crude oil having a very wide boiling range into constituent fractions with relatively narrow boiling range. These fractions are subsequently diverted to other refinery units as shown in FIG. 1 in accordance with the product pattern for further physical or chemical processing. The accompanying Table I summarizes process input and outputs for the Crude Still which is of conventional commercial design.

Desalted crude oil is successively heated via heat exchange with sidestream fractions and in a gas-fired pipe still heater. This operates on a once-through basis and is the principal source of heat input for crude distillation. The maximum temperature of material exiting the heater is determined by the bottoms temperature desired in the crude still which in turn is dictated by the thermal stability or coking tendencies of the residual oil. Tube wall temperatures in the pipe still heater are also limited to minimize coking.

Low boiling constituents in the crude oil are distilled overhead in the Crude Still, cooled to separate components condensable at atmospheric pressure, then compressed for further processing in the Gas Separation Unit.

Intermediate boiling components in the crude oil are removed as side-streams from the Crude Still. Certain of these side-stream fractions are processed in side-stream stripping columns to remove a portion of the lower boiling components and, in effect, to drive these up the column. Steam, superheated at 50 p.s.i.g. in gas-fired heaters, is used as a stripping agent. These side-stream fractions are partially cooled via heat exchange with the incoming crude oil.

The high-boiling bottoms stream from the Crude Still is fed directly to the Vacuum Still without intermediate cooling. Superheated steam is fed to the bottom of the Crude Still to function as a stripping agent and to reduce partial pressure of hydrocarbons so as to reduce caking tendency.

Crude oil handling capacity of the Crude Unit is primarily a function of the total heat transfer surface and the liquid and vapor handling capacity of the atmospheric column and associated side-stream strippers. This crude

still unit is designed for processing combined crudes with an average API gravity of about 35.5°.

TABLE I

Crude Still

5	Input
	Crude oil
	Stripping Steam
	Output
10	Non-condensed gases (C-4's and lower)
	C-5/160 to gasoline pool
	160/220 to reformer
	220/285 to reformer
	285/350 to jet fuel pool, pyrolysis unit
15	350/400 to jet fuel pool, pyrolysis unit
	400/430 to jet fuel pool
	430/525 to jet fuel pool, pyrolysis unit
	525/650 to pyrolysis unit and cat. cracker
	650+ to vacuum still

(2) Vacuum Distillation

The Vacuum Still is of conventional commercial design and separates the reduced crude oil into a distillate fraction and a higher-boiling residual fraction. In the refinery arrangement of this invention, the heavy gas oil distillate with boiling range of 650-1000° F., is to be cracked in the Catalytic Cracking Unit and the heavy residue is to be cracked thermally in the Delayed Coking Unit. The accompanying Table II summarizes the process inputs and outputs for the Vacuum Still.

The heat required for the vacuum distillation is derived from the heat content of the Crude Still bottoms at 600-700° F. plus heat added in a gas-fired pipe still heater. Maximum temperatures of streams exiting the heater and maximum tube wall temperatures are a function of the tendency of the reduced crude to break down thermally at the hold-up conditions in the heater and vacuum column. Maximum oil temperatures are generally in the range 700-800° F.

Operating pressure of the Vacuum Still is also a function of characteristics of the reduced crude. The column operates at about one-half atmosphere pressure. Partial pressure of hydrocarbons is further reduced by admitting live, superheated steam to the column.

Overhead material from the Vacuum Still is condensed by heat exchange with crude oil feed to the Crude Still and temperature further reduced in an air-cooled exchange. This distillate is a heavy gas oil with a boiling range of 650-1000° F., expressed as atmospheric boiling range, though actually measured at reduced pressure.

The Vacuum Still and Crude Still normally operate as an integrated equipment pair, and the bottoms from the Vacuum Still are fed directly to the Coking Unit.

The heavy gas oil distillate is blended with gas oils recovered from the Coking Unit and the combined stream used as feedstock for the Catalytic Cracking Unit.

The Vacuum Still is designed as a unit integrated with the Crude Still design. Design requirements of these units are a function of overall feed rate to the Refinery and of the crude oil characteristics.

TABLE II

Vacuum Still

65	Input
	Reduced crude from Crude Still
	Steam—superheated at 50 p.s.i.g.
	Output
70	650/1000 heavy gas oil to cat. cracker
	1000+ residue to delayed coker

(3) Delayed Coking

The Coking Unit which is of conventional commercial design processes the combination of residuum (1000+)

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from the Vacuum Still, a heavy fraction (650+) from the Pyrolysis quench system, and heavy cycle oil from Catalytic Cracking. Coking is essentially the process of thermally cracking at high temperature and extended hold-up time these high-boiling materials into lower molecular weight constituents which are suitable for processing elsewhere in the refinery and a non-volatile residue designated "green coke."

The green coke has applications as fuel, and it may also be calcined to yield a product suitable for manufacture of electrodes as used in the aluminum industry.

The combined feed stream to the delayed coker unit is fed to the bottom section of a fractionator where it exchanges heat with vapors from hot coke drum effluent. The heavy gas oil from the crude still column is also fed to a coker fractionating column where it is essentially totally vaporized by exchange of heat with the hot vapors exiting a coke drum in known conventional manner. The combined fresh feed and heavy recycle fraction are heated to the 900–1000° F. cracking temperature range in a gas-fired heater. Hold-up time at 800–850° F. is provided in one of two large coke drums where thermal breakdown occurs and coke is deposited. Operating pressure is about 10–50 p.s.i.g. In the usual operating cycle one coke drum is on stream for about a day. Meanwhile accumulated coke is discharged from the other. The heavy residue from the fractionator is recycled to extinction. Superheated, 200 p.s.i. steam is injected into the heater in order to reduce partial pressure.

The effluent from the coke drum is returned to the distillation column which operate at about 5–10 p.s.i.g. Non-condensable overhead gases are compressed for delivery to the Light Hydrocarbons Separation Unit. The column is operated to produce an overhead naphtha stream (C5/400) and a side-stream gas oil fraction (400/900). The naphtha is further processed in a Hydrotreater for sulfur removal before it is directed to the Reformer. The gas oil fractions are a part of the feed to Catalytic Cracking.

Normally, the Coking Unit is operated as an integral part of the crude oil processing facilities (with the Crude and Vacuum Stills). Similarly, the Thermal Naphtha Hydrotreater is operated in close sequence with the Coking Unit. The 400/650 and 650/900 gas oil fractions are directed to the Catalytic Cracking Unit with the S. R. 650/1000 heavy gas oil.

TABLE III

Delayed Coking Unit

Input	
	Residuum from Vacuum Still
	650+ residue from Pyrolysis quench
	Heavy cycle oil from Catalytic Cracking Steam
Output	
	Non-condensed gases (C-4's and lower)
	C-5/400 to Thermal Naphtha Hydrotreater
	400/650 to Catalytic Cracking
	650/900 to Catalytic Cracking
	Green coke

(4) Thermal Naphtha Hydrotreater

Naphtha from the Delayed Coker comprises high concentrations of unsaturated hydrocarbons plus sulfur- and nitrogen-containing components. This calls for a hydrotreating step to render the material suitable to feed the BTX Reformer.

Hydrotreatment is basically a hydrogenation carried out at 250–750 p.s.i.g. and 600–750° F. over a fixed bed catalyst. Because heat effects upon hydrogenating the olefins and diolefins are relatively large, the reaction is carried out in two stages. In the first reactor operating at less than 450° F. and with liquid phase, temperature control is achieved by recycle of cold product equivalent to about 50% of the feed. In the second reactor, operating at more severe, gas-phase conditions (up to 750° F.), 75

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hydrogenation is completed and the S- and N-containing materials broken down to form H₂S and NH₃.

Hydrogen is separated from the reactor effluent at intermediate pressure and recycled to the reaction system. A part of this gas is purged to prevent inerts build-up. The hydrotreated liquid is combined with product from the Straight Run Naphtha Hydrotreater for stripping of dissolved gas and low boilers before further processing in the BTX reformer.

The inputs and outputs of this unit are summarized in the following Table IV.

TABLE IV

Thermal Naphtha Hydrotreating

Input	
	C-5/400 from Coker
	Hydrogen
Output	
	Non-condensed gases (C-4 and lower)
	C-5/160 to Gasoline Pool
	160/285 to Reformer
	285/400 to Pyrolysis unit

(5) Catalytic Cracking

The Catalytic Cracking unit which is of known conventional design converts heavy gas oils to high octane motor gasoline and distillate products. In the reactor, some coke is formed as a byproduct of the reaction and is deposited on the catalyst. The catalyst is circulated continuously between the reactor and a regenerator where the coke is removed by burning to restore activity. The accompanying Table V summarizes inputs and outputs for this unit.

Both the reactor and the regenerator operate with finely divided catalyst maintained in a fluidized state by action of the hydrocarbon vapors and combustion air passing through the catalyst in corresponding vessels. Flow of catalyst between vessels is accomplished by a combination of gravity and pneumatic transport. Steam is used to purge the catalyst of combustion air and hydrocarbons as it moves between the vessels. Cyclone separators located within the vessels serve to minimize catalyst loss with the exit gases. A zeolite type catalyst will be used to attain a high conversion level. Silica alumina catalyst can also be used where lower conversion levels, 55–70%, is desired.

The off-gas from the regenerator is at a temperature level of 1200–1300° F. and rich in carbon monoxide as a result of the conditions maintained in the regeneration step. To recover this heat potential, the unit is equipped with a CO boiler which operates with an additional air feed as required to achieve substantially complete combustion. Steam is generated in this unit.

The hot vapors from the reactor are fed to a primary fractionator from which these cuts are produced: Non-condenser gases, H₂ through C₄'s to Gas Separation Light gasoline distillate, C₅'s+ to Alkylation Heavy gasoline sidestreams, to gasoline pool Light cycle oil sidestream, to Hydrocracker Heavy cycle oil bottoms, to Delayer Coker

TABLE V

Catalytic Cracking

Input	
	525/650 S. R. gas oil
	650/1000 S. R. gas oil
	400/650 Coker gas oil
	650/900 Coker gas oil
Output	
	C-2 and lighter to Gas Recovery
	C-3/C-4 to Gas Recovery
	Light gasoline to Alkylation
	Heavy gasoline
	Light cycle oil to Hydrocracker
	Heavy cycle oil to Delayed Coker

(6) Hydrocracking

The preferred hydrocracking process, which is generally known and commercially available, converts distillate fuel oils to lower boiling materials by cracking and hydrogenation at elevated temperature and pressure over a fixed bed catalyst. The process is particularly useful for upgrading heavy, naphthenic oils into lower molecular weight fractions suitable for reforming to aromatics. The Hydrocracker breaks down a light cycle oil from catalytic cracking and a 300/650 fraction recycled from the Pyrolysis unit. The extent of cracking required from this process step will be of a relatively low order.

The Hydrocracker operates at 1500–2500 p.s.i.g. and at temperatures from 700–900° F. Heat is supplied via heat exchange and gas-fired heaters. Because of the hydrogenation which occurs, the overall cracking-hydrogenation step is exothermic. Temperature control in the reactor is achieved by injection of cold-shot hydrogen at appropriate points. The reactor effluent is cooled by heat exchange and air cooling to 150° F. and flashed to 200 p.s.i.g. at which hydrogen is separated for recycle.

Nickel-tungsten sulfide on alumina and palladium on alumina are among the types of suitable catalysts and are available commercially. Regeneration involving air oxidation of deposited carbon, is required at about six month intervals. In addition to cracking and hydrogenation, the hydrocracking catalysts serve to convert a major part of the sulfur and nitrogen in the feedstream to H₂S and NH₃.

Cracked hydrocarbons from the recycle hydrogen separator are fed to a stabilizer operating at 175 p.s.i.g. for separation of light ends. Non-condensibles from the stabilizer (C₄ and lower) are directed to Light Hydrocarbons Separation; C-5/160 light ends are directed to the premium gasoline pool. Stabilizer bottoms are further fractionated in a second still into a 160/285 naphtha heads cut and a gas oil sidestream. The naphtha fraction is further processed in the reformer for aromatics production. The gas oil sidestream from the second column, with a 285/400 boiling range, serves as a part of the feed to the Pyrolysis unit. Bottoms from this column are mixed with fresh feed and recycled to extinction. Steam is fed to a side-stream stripper to separate low boilers from the 285/400 gas oil fraction. Steam is fed to the bottom of the still column as a stripping agent and to reduce hydrocarbon partial pressure. Gas-fired heaters are preferably used with each still.

Hydrogen make-up to Hydrocracking is preferably high-purity to minimize compression costs. Recycle hydrogen from the effluent separator is scrubbed with water at 200 p.s.i.g. to cool the gas before recompression and to remove H₂S and NH₃ formed in the reaction. A continuous purge from the system is required to control the concentration levels of methane and ethane in the system.

TABLE VI

Hydrocracking

Input	
430/525 straight run	
Light cycle oil from Cat. Cracker	
300/650 gas oil from Pyrolysis unit	
Hydrogen	
Output	
C-4 and lighter	
C-5/160 to premium gasoline	
160/285 to Catalytic Reformer	
285/400 to Pyrolysis unit	

(7) Light Hydrocarbons Separation (Gas Plant)

Gases and unstabilized liquids from the following processing units are charged to one of two Light Hydro-

carbons Separation Units for separation of the principal constituents to provide for their optimum utilization.

Saturated Gas Recovery

5	Crude Distillation*
	Hydrocracking
	Thermal Naphtha Hydrotreating
	Catalytic Reforming
10	Straight Run Naphtha Hydrotreating
	Pyrolysis Naphtha Hydrotreating
	Toluene Dealkylation
	Xylene Isomerization

Unsaturated Gas Recovery

15	Delayed Coker*
	Catalytic Cracking*

The accompanying Table VII summarizes inputs and outputs for this unit or step.

Gases produced at or near atmospheric pressure, as noted above by "*", are compressed to separation pressure, in the range 250–400 p.s.i.g. In those processes operating under pressure, gas separator pressure and operating pressures of stabilizers are determined by the pressure at which the Light Hydrocarbons Separation steps will be operating. The Separation steps will be similar in pattern, though processing saturated and unsaturated gases, respectively.

The compressed gases and an unstabilized (with respect to low boiler content) gasoline or naphtha fraction are charged to an absorber equipped with a reboiler to strip low boilers from the liquid fraction. The absorber is fed with stabilized gasoline or naphtha to serve as the primary absorbent and with a gas oil fraction supplied to the top section and removed as a sidestream. The gas oil serves to recover the gasoline or naphtha which would otherwise be lost with the tail gas. The rich gas oil is returned to the appropriate primary fractionator for separation of volatile from higher boiling constituents.

Tails streams from the absorbers are routed, to debutanizers to remove C-4's. The C-4 fractions are, in turn, routed to depropanizers.

C-3s from the unsaturated Hydrocarbons Separation system are routed to a propylene splitter which preferably will produce as a heads cut 92+ % propylene. This is combined with the propylene from Olefins Purification for removal from the Refinery for further handling.

Propane from the saturated Hydrocarbons Separation system is returned to the Pyrolysis unit. C-4 bottoms streams from the depropanizer are combined and routed to Alkylation.

TABLE VII

Light Hydrocarbons Recovery

55	Input
	Total saturated gases from process steps noted above in this section.
	Total unsaturated gases from process steps noted above in this section.
60	Output
	C-2 and lighter to Ethylene Purification
65	Propylene (92%)
	Propane—Recycle to Pyrolysis Unit
	Mixed Butenes—to Alkylation
	Mixed Butanes—to Alkylation
	Fuel gas
70	(8) C-4 and C-5 Alkylation

As is known, alkylation processes entail the reaction of olefins with isobutane in the presence of strong acid catalysts to produce higher molecular weight, branched-chain hydrocarbons. Most known oil refinery arrange-

ments use alkylation units to upgrade propylene, butylenes, and amylenes to products having good octane properties and boiling in the gasoline range. The refinery arrangement of this invention utilizes a conventional known Alkylation Unit to process butylenes and pentenes produced in Catalytic Cracking and the butylenes recovered from pyrolysis gases. The accompanying Table VIII summarizes the inputs and outputs of this unit.

Feed to the Alkylation Unit is limited to the isobutane, butylenes and C-5s. Because the amylenes are produced from the Catalytic Cracker as a mixture with C-6s and heavier, the stream is routed to a depentanizing column. The overhead C-5s from his column, comprising pentanes and pentenes, then serves as a part of the feed to Alkylation. The C-6+ bottoms from the depentanizer go directly to the gasoline pool.

The combined hydrocarbon feed streams are processed through activated alumina driers to remove trace quantities of water. It is important that the reaction system be kept free of water as a step to minimizing corrosion, and achieving high yields in reaction.

Either hydrofluoric acid or sulfuric acid can be used as the catalyst for alkylation processes. Hydrofluoric acid catalyst is preferably used in the refinery arrangement of this invention. The reaction is carried out in the liquid phase at about 100° F. and moderate pressure, sufficient to maintain reactants in the liquid phase. The reaction is strongly exothermic so that heat must be removed via internal cooling coils.

The ratio of isobutane to olefin in the feed stream is generally maintained above 3/1 on a molar basis. Yields and octane number of the product are improved at the higher feed ratios, though at a penalty in operating cost.

The reactor effluent is separated into a light, hydrocarbon layer and a heavier, acid layer in a simple gravity separator. Excess isobutane is distilled from the alkylate product and recycled to the reaction step. A portion of this isobutane is processed in a second still to separate propane introduced with the feed which would otherwise build up in the system. HF contained in the propane stream is recovered in an HF stripper and the propane bottoms routed to the plant fuel gas system.

The product alkylate is produced as bottoms from the deisobutanizer. This stream is washed with aqueous caustic and routed to storage.

A small amount of acid soluble, hydrocarbon acid adducts are formed in the process. These materials are to be separated from the HF in an acid stripper wherein the HF is distilled overhead and the acid oils purged as a bottoms stream.

TABLE VII

C-3/C-4 Alkylation

Input	
Mixed Butenes—	from Butadiene Recovery
Mixed Butenes—	from Unsat. Lt. H. C. Rec.
Mixed Butanes—	from Sat. Lt. H.C. Rec.
Purchased Isobutane	
Lt. Cat. Gasoline—	from Cat. Cracker
Output	
C-4 Alkylate—	to Gasoline Pool
C-5 Alkylate (+Pentanes)	to Gasoline Pool
Depentanized Gasoline—	to Gasoline Pool
Normal Butane—	to Gasoline Pool

(9) Straight-Run Naphtha Hydrotreater

Naphtha, 160/285, from the Crude Unit contains small concentrations of sulfur and nitrogen which must be removed before this material is processed in Catalytic Reforming to produce aromatics. The hydrotreatment is essentially a mild cracking to break down the S and N containing components in the presence of hydrogen so that impurities are removed as H₂S and NH₃.

The hydrotreating reaction preferably is carried out in a hydrogen environment over a fixed-bed cobalt-molybdenum catalyst at temperatures in the range, 600–750° F., and pressures of 250–750 p.s.i.g. Ingredients are brought to reaction temperature by a combination of heat exchange with reactor effluent and a gas-fired heater.

Effluent from the reactor is processed through a gas-liquid separator and then a stabilizer which serves to strip out low boiling components before the naphtha is fed to the Catalytic Reformer.

Hydrogen and low-boiling hydrocarbons purged from the system are to be fed to the plant fuel gas system after sulfur recovery.

The Hydrotreater will be operating in close sequence with the Catalytic Reformer. The inputs and outputs for this unit are summarized in the following Table IX.

TABLE IX

Straight-Run Naphtha Hydrotreater

Input	
160/285 Naphtha—	from Crude Still
Hydrogen	
Output	
Desulfurized Naphtha—	to Cat. Reformer
Off-gas (about 82% H ₂ and 5% H ₂ S)—	to H ₂ S Recovery

(10) Catalytic Reforming

The Catalytic Reforming step is a well-known process; it converts naphthenic hydrocarbons to aromatics by a dehydrogenation mechanism. At the same time, but to a much lesser extent, straight chain C-6 to C-9 hydrocarbons are isomerized and dehydrogenated to form aromatics. This process is used in most oil refineries to produce high octane components for use in gasoline. In the refinery arrangement of this invention, Catalytic Reforming will be used to maximize output of benzene, toluene and xylenes with inputs and outputs summarized in following Table X.

Feed to Reformer is first processed in a single column to separate isohexane. This distillation is necessary to preserve all possible benzene precursors in the naphtha while not subjecting the high octane isohexane to cracking in the reformer. About 50% of the isohexane (B.P. 140, 146° F.) and 80% of the n-hexane (B.P. 156° F.) remains in the deisohexanizer bottoms.

The reforming reactions are carried out under moderate pressure, about 250 p.s.i.g., and elevated temperature over supported platinum catalyst in fixed bed reactors. Because the reaction is endothermic, it is necessary to distribute the overall reaction over a succession of reactors with provisions for reheating the process stream between reactors. In practice, temperature may be increased from 900 to 930° F. as the material flows through the succession of reactors.

To minimize the tendency for accumulation of high molecular weight condensation products, hydrogen is introduced to the reactor train with the naphtha feed stream. In spite of this feature, the process is characterized by deposition of coke on the catalyst which calls for periodic regeneration by oxidation.

The reactor effluent is cooled and let down to 250 p.s.i.g. separator pressure. Hydrogen produced in the reforming reaction is separated as an 85% stream mixed with methane and ethane. A portion of this hydrogen is recycled to the reactor train, as noted above.

Liquid from the hydrogen separator is fed to the stabilizer which produces a C-4 and lighter non-condensable fraction and a C-5/160 distillate. These streams are directed to the Gas Separation Plant and the gasoline pool, respectively. The 160+ bottoms from the stabilizer contain 30–40% of benzene, toluene, and xylene. These aromatics are recovered by extraction as discussed in following Section 11 relating to Aromatics Extraction.

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TABLE X

Catalytic Reforming

Input	
160/285 Straight Run	
160/285 from Hydrocracker	
160/285 from Coker	
Raffinate from Pyrolysis Extraction	
Output	
C-5/160 to Gasoline Pool	
160+ to Extraction	
Hydrogen from Separator	
C-4 and lower ex Stabilizer (54% H ₂)	

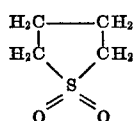
(11) Aromatics Extraction

The refinery arrangement of this invention makes use of two separate units for solvent extraction of aromatics from C-6 to C-9 fractions. The larger of these units processes the effluent from Catalytic Reforming. The smaller, processes the pyrolysis liquid fraction after hydrotreating. Two units instead of one makes possible optimum efficiency in a situation wherein BTX distribution will be different for the two feed streams as noted in this approximate comparison.

	Percent	
	Reformate	Pyrolysis Liquids
Benzene.....	9	23
Toluene.....	16	13
Xylene.....	30	9
C-9 aromatics.....	5	15
Raffinate.....	40	40
Total.....	100	100

Inputs and outputs for the two units are summarized in the accompanying Table XI.

The known Sulfolane process, which is commercially licensed by the Universal Oil Products Company under arrangements made with the Shell Development Company, preferably is used for extracting aromatics from the mixed C-6/C-9 streams. Sulfolane is a heterocyclic sulfone with the formula:



and boiling at 549° F., freezing at 82° F.

The hydrocarbon feed stream is contacted with the Sulfolane solvent at a relatively high solvent/hydrocarbon ratio (7/1) in a rotating disc contactor device which is also a known commercialized development of Shell. In this extraction process, the circulating lean solvent contains 1.5-2% water. The extract is subjected to partial stripping to separate an aromatics stream for refluxing to the rotating disc contactor device. A final steam stripping operation separates the mixed aromatics from the polar solvent. After decanting contained water, the aromatic distillate streams from the two units are combined and routed to BTX Distillation to recover benzene, toluene, and xylene.

The paraffinic raffinate from the rotating disc contactor device is washed with water in order to recover entrained Sulfolane for recycle to the extraction system.

The water stream is returned to the system via the stripping column. A part of the C-6/C-8 raffinate, which will derive from the reformate, serves as feedstock to the Pyrolysis unit; the balance goes to the gasoline pool. Raffinate from extraction of pyrolysis liquids is relatively rich in naphthanes and is therefore routed

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to Catalytic Reforming to utilize the aromatics potential of this stream.

TABLE XI

Aromatics Extraction

5	Input	
	160+ from Reformer	
	C-6+ from Pyrolysis Naphtha Hydrotreating	
	Output	
10	Heavy Reformate Raffinate—to Pyrolysis	
	Light Reformate Raffinate—to Gasoline Pool	
	Pyrolysis Naphtha Raffinate—to Reformer	
	BTX Extract—from Reformate	
	BTX Extract—from Pyrolysis Naphtha	

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(12) Pyrolysis—Steam Cracking, Ethylene and Propylene Producing Plant

The refinery arrangement of this invention is provided with a steam cracking pyrolysis unit for producing ethylene and propylene, among other products, which unit operates, for the most part, with liquid feedstocks, naphthas, and gas oils, which are derived from Crude Distillation, Hydrocracking, and Aromatics Extraction. Table XII summarizes inputs and outputs for this unit.

The Pyrolysis unit facilities comprises three types of furnaces to process the various feed fractions in accordance with the approximate distribution of inputs noted in Table XII.

The ethane/propane furnaces are designed for short contact time and high exit temperature (1520-1550° F.) in order to achieve about 60% ethane conversion per pass. Propane conversion at these conditions is about 90% per pass. Ethylene production is about 43 lbs./100 lbs feed gas. About 0.3 lb. steam is added per lb. of feed gas stream in order to reduce the partial pressure of the hydrocarbons and in turn to reduce the tendency to coke formation.

The furnaces processing feedstocks ranging from C-4s to naphtha operate with shorter residence time and with a lower exit temperature (1350 to 1450° F.). Conversion per pass is on the order of 95%. At this conversion level, ethylene production is 29-30 lbs./100 lbs. hydrocarbon feed. Steam is added to these cracking furnaces at the rate of 0.5 lb./lb. hydrocarbon feed in order to suppress coking.

The furnaces which process the heavy naphtha and gas oil are similar in design to the units operating on C-4/naphtha feedstock. Contact time is in the range .15 to .25 second and exit temperature is in the range 1350 to 1500° F. At these conditions about 20 lbs. ethylene are produced per 100 lbs. hydrocarbon feed.

The cracking furnaces operate with transfer line exchangers to quench the exit gas and to generate high pressure steam. The pressure at which steam is generated will be in the range (650 to 1800 p.s.i.g.).

The hot gases from the transfer line exchangers are further cooled by contact with oil circulating through a quench tower. This quench system is independent of that used for effluent from the ethane/propane cracking furnaces. The hot circulating oil is used to generate 200 p.s.i.g. steam and is further cooled by means of air exchangers. A bottoms stream from the quench tower is returned to the coker. A sidestream from the tower is steam-stripped and returned to the Hydrocracker.

The hot gases exiting the transfer line exchangers of the ethane/propane furnaces are combined with the gas exit the oil quench tower and further cooled in the water quench tower. This second tower operates with a combination of air and water cooling. A part of the hydrocarbon liquids condensed in the water quench are recycled to serve as reflux to the oil quench tower. The net liquid production is stripped of its C-4s content and is further processed via hydrotreating and extraction for recovery of its aromatics content.

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TABLE XII

Pyrolysis Unit

Input

Recycle Ethane
Propane—from Light Hydrocarbon Sepn
C-5—from Pyrolysis Naphtha Hydrotreating
Raffinate—from Reformate Aromatics Extrusion
285/400—Straight Run Naphtha
285/400—Hydrocracker Naphtha
285/400—Coker Naphtha
430/650—Straight Run Gas Oil

Output

H₂/300+—to Pyrolysis products separation or Ethylene Purification unit
300/650—Gas Oil to Hydrocracker
650+—to Delayed Coker

(13) Ethylene Purification, or Pyrolysis Products Separation Unit

Mixed gases from the Pyrolysis unit are compressed and separated by fractionation into the following principal components: Hydrogen, methane, ethylene, ethane, propylene, mixed C-4's and C-5's and higher. Water vapor, CO₂ and H₂S, and acetylenes are also separated as part of the purification step. The C-2 and lower gas fraction from Catalytic Cracking is also processed through Ethylene Purification in combination with the gases from Pyrolysis in order to separate the components for effective utilization. The process gases are compressed and refrigerated via propylene and ethylene refrigeration systems. A further degree of refrigeration is achieved via expansion of hydrogen separated in the process. Table XIII summarizes input and output for the step or unit.

The gases from the pyrolysis unit water quench tower are compressed by means of a steam turbine-driven centrifugal compressor comprising four stages in two or more separate cases. Liquids (C-4 and higher) which are condensed in the interstage coolers are combined with the naphtha from the quench system for further processing.

Between the third and fourth stages of compression, the gas stream is subjected to monoethanol amine scrubbing and a caustic wash to remove acid gases. The CO₂ and H₂S separated are routed from the amine regeneration to the Sulfur Recovery Unit. A final water wash serves to remove traces of caustic carryover.

After final compression to the order of 550 p.s.i.g., residual water is removed from the gas stream in an activated alumina dryer to insure against ice formation in subsequent stages of the process.

In addition to the charge compressor noted above, the Ethylene Recovery unit utilizes large centrifugal compressors as the main features of the propylene and ethylene refrigeration systems.

The bone-dry gas stream is cooled successively by heat exchange with propylene from the C-3 refrigeration system and with hydrogen and methane, chilled by reversible expansion through a turbo-expander. The chilled gases are passed first through a demethanizing column to remove hydrogen and methane. Reflux to this column is achieved by heat exchange against vaporizing ethylene from the C-2 refrigeration system. Boil-up is provided by condensing propylene vapor in the reboiler. The separation system is designed with the heat exchange facilities necessary for liquefying the methane to enable separating hydrogen at a 94-96% purity level for delivery to hydrogen consuming processes elsewhere in the refinery arrangement. The methane is revaporized and routed to the fuel gas distribution system.

Tails from the demethanizer serve as feed to the deethanizing column. Here, the ethane and ethylene are overhead, with reflux provided by propylene refrigeration and boil-up provided by heat exchange against cooling water or condensing steam.

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Acetylene contained in the overhead from the deethanizer is removed by selective hydrogenation over a supported nickel catalyst. Acetylene removal is deferred to this point in the process in order to minimize the extent of butadiene hydrogenation which would otherwise occur if the total gas stream were passed over the hydrogenation catalyst. Following acetylene removal, the gas is processed through a secondary demethanizing column in order to remove the small amount of unreacted hydrogen and associated methane. Refined ethylene is finally taken overhead in the C-2 splitter. Ethane tails are heated by exchange against process streams and recycled to the Pyrolysis unit.

The tails stream from the deethanizer is separated in the depropanizer into a C-3 overhead fraction and a C-4+ bottoms stream. Methyl acetylene and propadiene in the C-3 stream are removed via a second selective hydrogenation step over a supported nickel catalyst. The excess hydrogen and associated methane are taken overhead from the C-3 stream in a propylene stripper.

Propylene produced via this recovery scheme contains about 8-12% propane deriving from the propane produced in the Pyrolysis step.

Propylene is also produced in the refinery arrangement of this invention as one of the light hydrocarbons from the Catalytic Cracking step. In this case, the concentration of propylene in the combined C-3 stream is of an order to require installation of a propylene fractionator. Propylene overhead from the fractionator (about 92% conc.) is combined with the propylene from the Ethylene Purification unit and the combined stream removed from the Refinery as product. Propane tails from the fractionator are routed to the Pyrolysis unit. The propylene fractionator may be located either in a part of the Light Hydrocarbons Separation unit or Ethylene Purification unit.

The tails stream from the depropanizer contains the C-4's and higher. This material is processed through a debutanizing column and the C-4 fraction taken overhead. The bottoms stream, C-5 and higher, is combined with the pyrolysis naphtha separated in the quench and compression systems, and the mixture routed to Pyrolysis Naphtha Hydrotreating. The C-4 overhead stream from the debutanizer contains 40-50% butadiene, 55-45% butenes and is routed to the Butadiene Recovery unit.

TABLE XIII

Ethylene purification or pyrolysis products separation

Input

H₂/300—from Pyrolysis
H₂/C₂—from Catalytic Cracker

Output

Hydrogen
Fuel Gas (5.3% H₂, 1.2% ethylene)
Ethylene
Ethane—Recycle to Pyrolysis
Propylene (89%)
Mixed C-4's—To Butadiene Recovery
C-S/300—to Hydrotreating

(14) Butadiene Recovery

Butadiene is recovered from the C-4 mixture produced in the Ethylene Purification step by a combination of extractive distillation and distillation. The known patented process based on acetonitrile (ACN) as an extraction solvent is utilized. The effect of distillation in a system containing ACN is illustrated in this tabulation:

RELATIVE ORDER OF VOLATILITY

No solvent	B.P. (° F.)	With ACN
70 1-Butene.....	10.9	1-Butene.
1-Butene.....	19.6	n-Butene.
Butene-1.....	20.7	1-Butene.
1,3-butadiene.....	24.1	Butene-1.
n-Butene.....	31.1	trans Butene-2.
trans Butene-2.....	33.6	cis Butene-2.
cis Butene-2.....	38.7	1,3-butadiene.
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The accompanying Table XIV summarizes inputs and outputs for this unit or step.

The C-4 mixture is first passed through a vapor phase hydrogenation step operating at 100 p.s.i.g. and ca. 350° C. to remove acetylenic compounds. The reactor effluent is condensed and fed to the extractive distillation column which contains 130 plates and operates at 85 p.s.i.g. with a solvent/C-4 feed ratio of 7/1. A water solution of 90% acetonitrile is used as the extraction solvent. Butanes, butene-1 and isobutene are distilled overhead at a 10/1 L/D. Butadiene and butene-2 are stripped from the butadiene-rich solvent in a 40-plate stripping column. The lean water/ACN solvent is cooled and returned to the extractive distillation column. Distillate from the stripper is split into a refined butadiene overhead stream and a butene-2 tails cut in a final 160 plate column. C-3's and excess hydrogen are vented as non-condensables from the purification column. The refined butadiene is stored under pressure pending removal from the plant.

The butene-2 bottoms stream from the purification column and the butene-1 and isobutene distillate from the extractive distillation column are combined and washed with water to remove small quantities of acetonitrile which distill overhead in the extractive distillation and solvent stripping columns. Water from the wash column is fed to a 20-plate still where a water/ACN azeotrope is taken overhead for return to the extraction system. High boilers and salts that would otherwise accumulate in the extraction solvent are removed by feeding continuously a slip stream from the extraction system to the ACN recovery column. The mixed butenes, after separation of butadiene, are used as a part of the feed to C-4 and C-5 alkylation.

TABLE XIV

Butadiene Recovery

Input
Mixed C-4's—from Pyrolysis
Output
Butadiene
Mixed Butenes—to Alkylation

(15) Pyrolysis Naphtha Hydrotreater

The purpose of hydrotreating the C-5 to C-9 liquids recovered from Pyrolysis is to hydrogenate catalytically the diolefins, olefins and any acetylenic compounds contained. This is to (a) prevent polymerization of the dienes and consequent formation of gums in subsequent processing steps, and (b) to facilitate separation of aromatics from paraffins via extraction. A second function of Hydrotreating is to remove sulfur compounds from the aromatics fraction as H₂S. Inputs and outputs for this well-known conventional process unit are summarized in the accompanying Table XV.

The C-5+ liquids from Pyrolysis are pressured to 900 p.s.i.g., heated in a reactor to reaction temperature (400–700° F.) by a combination of heat exchange and fired heater. The preheated liquid-hydrogen mixture is passed over a fixed bed catalyst where the extent of reaction accounts for a 30–75° F. temperature rise. Reaction conditions are selected to maintain mixed gas/liquid phases in the reactor and thereby to minimize problems deriving from disposition of diene polymer on the catalyst.

Affluent from the reactor is cooled, hydrogen separated for recycle, and liquids fed to a two column train comprising depentanizer and fractionator. Light ends from the depentanizer are recycled to the Pyrolysis unit. The fractionator delivers a C-6/C-8 fraction overhead and a C-9+ fraction as bottoms. The C-6/C-8 fraction is fed to Aromatics Extraction and the C-9+ fraction to the gasoline pool.

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TABLE XV

Pyrolysis Naphtha Hydrotreating

Input
Naphtha from Ethylene Purification
Hydrogen
Output
C-5—Recycle to Pyrolysis
C-6/C-9—To BTX Extraction
Off Gas

(16) BTX Distillation

The aromatics recovered from the catalytic reformat and from the pyrolysis naphtha in the two extraction units are combined with effluent from Toluene Dealkylation and routed to BTX Distillation. Here, there is a simple distillation to separate the mixture into the benzene, toluene, and xylene components. Inputs and output for this process unit are summarized in the accompanying Table XVI.

The combined feed stream is fed to a benzene column and toluene column in sequence. Refined benzene and toluene are taken overhead from the respective columns. This process unit is provided with a third tower or column for separating a xylene cut from C-9 aromatics. The refinery arrangement of the invention is designed with this separation integrated with the preferred Para Xylene Isomerization and Recovery step. This process unit is also provided with clay treating towers which are used to remove residual olefins.

Benzene recovered in BTX Distillation is routed to Benzene Hydrogenation. Recovered toluene is used to produce additional benzene via Toluene Dealkylation. The xylenes and C-9 aromatics which constitute the tails stream from the toluene column are routed to Para Xylene Isomerization and Recovery.

TABLE XVI

BTX Distillation

Input
Aromatics—from Extraction
Benzene/Toluene—from ex Toluene Dealkylation
Output
Benzene
Benzene—to Hydrogenation
Toluene—
Toluene—to Toluene Dealkylation
Xylene—to Para Xylene Recovery
C-9 Aromatics—to Gasoline Pool

(17) Toluene Dealkylation

In the refinery arrangement of this invention and under current economic conditions toluene has a higher value as a precursor to benzene than as a component of motor gasoline, its principal alternative use. The known conventional Toluene Dealkylation unit provides a means for thermally dealkylating toluene in presence of hydrogen. The process involves partial conversion per pass and the reactor effluent is therefore returned to BTX Distillation for separation of the benzene and toluene components. Table XVII summarizes the inputs and outputs of this step or unit.

Toluene and hydrogen are pumped to 500–600 p.s.i.g. and heated to a reaction temperature of about 1300° C. in a gas-fired heater. The reaction is exothermic and actual reaction temperature is controlled via introduction of cold-shot hydrogen. Yield and conversion in the reaction step are a function of temperature, hold-up time, and hydrogen partial pressure. Hydrogen/toluene feed ratio is about 5/1 on a molar basis. Once-through conversion is in the range 70–90% and overall yield is of the order, 97–98%. A gas purge stream is required to maintain a hydrogen content of 50–70% in the cycle gas.

The reactor effluent is cooled and routed to a high pressure gas/liquid separator and a stabilizing column in sequence.

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The purge gas stream may be handled as desired, either (a) to route the hydrogen-rich gas to Hydrogen Manufacture where the methane content is steam-reformed, or (b) to route the hydrogen-rich gas to the Ethylene Purification unit for cryogenic purification along with the hydrogen formed in the Pyrolysis step.

The benzene-toluene mixture from the stabilizer is returned to BTX Distillation as part of the main feed stream to this unit.

TABLE XVII

Toluene Dealkylation

Input

Toluene—from BTX Distillation

Hydrogen

Output

B/T Mixture—to BTX Distillation

Off Gas (59% H₂)

(18) Benzene Hydrogenation

Benzene produced in a refinery arrangement of this invention is hydrogenated over a catalyst such as, for example, Raney nickel, at moderate pressure and temperature to produce cyclohexane in stoichiometric yields. Inputs and outputs for Benzene Hydrogenation unit, which is conventional and well-known, are summarized in the accompanying Table XVIII.

The nickel catalysts normally used for this hydrogenation are sulfur sensitive so that careful attention is required to ensure that process feed streams are free of sulfur compounds. The process streams which are to be sources of benzene are previously processed in hydrotreating steps which serve to remove sulfur to adequately low levels. The hydrogenation reaction is highly exothermic so that special steps are required to control reaction temperature. This unit preferably achieves temperature control by circulating a portion of the reacting liquid through an exchanger to generate low pressure steam. In this case, a final, finishing reactor is used to ensure complete conversion.

Reaction is carried out at 300–400 p.s.i.g. and 400–450° C. The reactor effluent is routed to a liquid-gas separator and stabilizing column to remove dissolved gases, and is then suitably pure for shipment.

TABLE XVIII

Benzene Hydrogenation

Input

Benzene—from BTX Distillation

Hydrogen

Output

Cyclohexane

Off gas (38% H₂)

(19) Para Xylene Separation

The xylenes/C-9 aromatics cut from BTX distillation contains each of the three xylene isomers plus ethyl benzene. The para xylene component is not readily separated by distillation, as is apparent from the respective boiling points, noted below. Further, it is desirable to increase the amount of recoverable para xylene. This is accomplished in an Isomerization step wherein the mixture of C-8 aromatics is subjected to a catalyzed isomerization to shift the composition toward an equilibrium mixture which is richer in para xylene content than the feed stream. Para xylene is separated from this mixture via crystallization.

	Boiling point (° F.)	Freezing point (° F.)
Ethyl benzene.....	277.1	−139.0
Para xylene.....	281.0	+55.9
Meta xylene.....	282.4	−54.2
Ortho xylene.....	291.9	−13.3
Cumene ¹	306.3	−140.9
1,2,3-trimethyl benzene ²	348.9	−13.7

¹ Lowest boiling of the C-9 aromatic isomers.

² Highest freezing of the C-9 aromatic isomers.

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The freezing points noted above are for the pure components. In practice, para xylene is separated from a eutectic mixture at temperatures of the order of −80 to −100° F. The filtrate containing para xylene still in solution plus the other C-8 compounds is returned to the isomerization step. Table XIX accompanying this section summarizes inputs and outputs for the Para Xylene Separation (Isomerization and Recovery) step or unit.

The isomerization of C-8 aromatics is accomplished by the following known process operated commercially in the U.S.

The make-up and recycle xylene streams are combined and pumped to reactor pressure and preheated to reactor temperature in a gas-fired heater. Hydrogen is supplied to the isomerization process in order to suppress coking in the catalyst bed. The isomerization reactor operates with a supported, precious metals catalyst in the temperature range, 700–800° F. at 200–300 p.s.i.g. As the catalyst ages, the extent of ethyl benzene isomerization will be the first to fall off, requiring gradual increase in reactor temperature to the point where a catalyst change is called for.

Effluent from the isomerization reactor is processed through a distillation train consisting of (1) a stabilizer for separation of dissolved gases and low boilers, (2) a benzene/toluene tower which produces a heads cut consisting of a small quantity of mixed benzene and toluene byproduct, and (3) a xylene column which makes the separation between the xylenes and the C-9 aromatics. The benzene/toluene cut is returned to BTX Distillation for recovery. The C-9 aromatics tails stream is routed to storage to serve as part of the gasoline pool.

The following known commercially available process is used for para xylene recovery. This involves drying the mixed xylene feed stream over a fixed-bed dessicant and chilling to crystallization temperatures in a succession of scraped-surface exchangers. Separation of filtrate from the para xylene crystals is accomplished in a continuous centrifuge. Filtrate from this separation is returned to the isomerization step. A quantity of relatively pure para xylene liquid from the third separation step is recycled to serve for repulping the crystals from the first stage separation and in so doing to reduce the impurities content of the para xylene crystals. A second centrifuge separates crystals from the repulping mother liquor. Filtrate from this separation is returned to the first stage crystallizers. Crystals from the second centrifuge are partially melted as a further purification measure and subjected to a third and final centrifugal separation. Filtrate from this separation is recycled for repulping purposes as noted above. The para xylene crystals from the third stage separation are melted and the liquid para xylene routed to storage prior to shipment.

Refrigeration for the crystallization step is accomplished via liquid ethylene evaporation.

TABLE XIX

Para Xylene Separation (Isomerization and Recovery)

Input

Mixed Xylenes—from BTX Distillation

Hydrogen

Output

Para Xylene

Benzene Toluene Mixture—to Gasoline Pool

Off-Gas (70% H₂)

(20) Hydrogen Generation

Hydrogen is produced in certain of the units of the refinery arrangement of this invention and is consumed in another group of process units as follows:

Produce Hydrogen:

Catalytic cracking

Catalytic reforming

Pyrolysis and ethylene purification

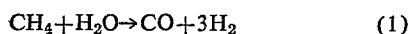
Delayed coking

Consume Hydrogen:

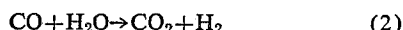
Straight-Run naphtha hydrotreating
 Coker naphtha hydrotreating
 Pyrolysis naphtha hydrotreating
 Hydrocracking
 Toluene dealkylation
 Para xylene isomerization
 Benzene hydrogenation

Hydrogen consumption for the seven process units noted above exceeds supply of byproduct hydrogen, which requires that a unit for Hydrogen Manufacture be included as a part of the refinery arrangement. This unit involves the familiar well-known process for reforming natural gas with steam. The accompanying Table XX summarizes the inputs and outputs of this unit.

Natural gas and certain refinery gas streams which are rich in hydrogen are mixed and fed with an excess of steam over a fixed bed catalyst contained in the vertical reformer tubes. The feed gas must be free of sulfur which would otherwise poison the catalyst. Operating pressure is in the range 100–300 p.s.i., dependent upon supply pressure of the natural gas and operating pressure of certain of the hydrogen consuming units. Reaction temperature will be in the range of 1500–1800° F. Heat for the reforming reaction is supplied via fuel gas combustion and transferred through the tube walls. The reforming reaction can be simply summarized as:

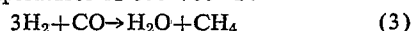


The product gases exit the reformer are cooled to the order of 500–600° F., mixed with an additional quantity of steam and passed over a second catalyst bed where the carbon monoxide is reacted with steam to produce carbon dioxide and additional hydrogen.



This is referred to as the "shift" reaction; it is exothermic, resulting in an appreciable temperature rise over the catalyst bed. The heat effect is moderated by maintaining an appreciable excess of steam in the reaction system. The excess steam also forces the reaction and minimizes carbon monoxide concentration in the product gases. The gases are cooled to condense out the major part of the water content, then routed to a scrubbing column for removal of carbon dioxide formed in the shift reaction. A water solution of monoethanol amine (MEA) is used preferably as an absorption medium. Application of heat to the rich MEA absorbent in a separate regeneration column drives the carbon dioxide overhead. The lean MEA absorbent from the regeneration column is cooled, repressured and returned to the scrubbing column.

The hydrogen, free of CO₂ following MEA scrubbing, contains a small amount of CO which is to be avoided in most hydrogenation reactions. This CO is removed by carrying out the "methanation" reaction with H₂ over a catalyst at a temperatures of 600–700° F.



This is the reverse of reaction (1) noted above. It is highly exothermic and requires attention to means of temperature control. This is usually accomplished by addition of cold-shot gas to the reactor. The purified hydrogen contains a small amount of CH₄ (about 5%) which is inert in the several processes consuming hydrogen in the refinery. The purified hydrogen is mixed with hydrogen from Ethylene Purification and routed to the various units in the refinery via a distribution system operating about 200–300 p.s.i.g.

TABLE U-1
 Hydrogen Generation

Input
 Methane
 Output
 Hydrogen
 Carbon Dioxide

(A) H₂S Separation and Sulfur Recovery

Gas streams from the following process units contain hydrogen sulfide in varying concentrations:

- 5 Straight Run Naphtha Hydrotreater
- Thermal Naphtha Hydrotreater
- Hydrocracker
- Delayed Coker

- 10 To remove this H₂S content, the gas streams are routed to a monoethanol amine (MEA) absorption system. Here the H₂S is scrubbed from the combined gas streams which are then directed to the Light Hydrocarbons Separation Unit. The rich MEA solution is regenerated in steam-heated regenerator from which the H₂S rich gas is routed to the Sulfur Recovery Unit. The regenerated MEA solution is cooled and returned to the absorption step.

(B) Sulfur Recovery

- 20 H₂S from the H₂S Separation Unit is combined with acid gases separated in the Ethylene Purification Unit and with acid gases from the sour water stripper and spent caustic neutralization unit. The combined gas stream is processed for conversion to elemental sulfur by means of the Claus process. In this unit the H₂S is subjected to partial combustion to form sulfur and water. Sulfur is condensed as the combustion gases are cooled and separated as a liquid. Unreacted H₂S is further reacted in two stages of catalytic oxidation to produce additional sulfur.

(22) Merox Treatment

- 30 This is a known conventional process step or unit licensed commercially by the U.O.P. Process Division of Universal Oil Products Company and used in the refinery arrangement of this invention to sweeten a combined straight run heat naphtha and light gas oil fractions directly used for jet fuel product by converting mercaptan to disulfides.

- 40 In this unit the combined fraction stream is contacted with caustic containing Merox catalyst to extract the mercaptans. The treated stream is treated with air and more Merox catalyst solution and settled. Merox catalyst solution used in the extraction step is mixed with air and regenerated in an oxidizer. Excess air and disulfides are removed overhead in respective separators. Merox catalyst solution is returned to the extraction step.

- 45 The previously described units, or process steps, are arranged and interrelated as shown in FIG. 1 and are further described in the individual descriptions of each unit.

- 50 The basic refinery arrangement connected for flow of material as shown by the unbroken and dashed lines of FIG. 1 represents a preferred embodiment of the invention which produces, in addition to the other products, gasolines which require lead additives such as tetraethyl lead to achieve the required octane ratings.

- 55 This same refinery arrangement, when connected for flow of material as shown by the unbroken and dotted lines represents another preferred embodiment for producing, in addition to the other products, gasolines which do not require the lead additives for use. This simple conversion, which does not require significant changes in the units or process steps themselves, is one indication of the high degree of flexibility possessed by the refinery arrangement of the invention.

- 65 Referring to the drawing, one important aspect of the refinery arrangement of this invention involves the high degree of interaction and cooperation between the ethylene and propylene producing means (which comprises pyrolysis unit capable of handling gas, naphtha and gas oil inputs, a pyrolysis products separation unit, and a pyrolysis naphtha hydrotreater unit, all not shown) and the other basic units of the arrangements. This contributes importantly to the ability of the arrangement to produce the varied slate of high value products in the most efficient manner.
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It will be seen in FIG. 1, referring to the arrangement for producing leaded gasoline, that the delayed coking unit, the catalytic cracking unit, the catalytic hydrocracker unit, the ethylene and propylene producing unit, and the catalytic (BTX) reforming unit all receive as inputs straight run fractions from the distillation units. In addition, a straight run light naphtha fraction from the distillation units is supplied directly to the gas plant, and portions of two straight run heavy naphtha fractions are combined with portions of two straight run light gas oil fractions to produce a stream directly usable as jet fuel, after the sweetening treatment (Merox unit). The pyrolysis unit of the ethylene and propylene producing unit receives, in addition to the straight run gas oil and straight run naphtha fractions from the distillation units, propane from the catalytic cracking unit (via the gas plant and propylene splitter units), naphtha and gas oil fractions from the hydrocracker unit, and certain naphtha fractions from the delayed coker unit. The pyrolysis unit (not shown) of the ethylene and propylene producing unit supplies its output to the pyrolysis products separation unit (not shown) of the ethylene and propylene producing unit. The pyrolysis products separation unit supplies output product streams of ethylene and propylene, an output stream comprising benzene, toluene, and xylenes to an aromatic products recovery unit, and an output stream comprising butadiene to a butadiene recovery unit. The pyrolysis product separation unit also receives a C₂ and lower gas fraction from the catalytic cracking unit and supplies byproduct streams comprising heavy gas oil and pyrolysis tar fractions to the delayed coking unit and comprising gas oil fractions to the hydrocracker unit. The BTX reformer or catalytic reformer unit shown in FIG. 1 receives two heavy naphtha fractions from the crude distillation unit after they have passed through a hydrotreater unit (Hydrodesulfurization unit, HDU), a naphtha fraction from the delayed coking unit after it has passed through a thermal naphtha hydrotreater, and naphtha fractions from the hydrocracker unit. The BTX reformer unit supplies a C₄ and lighter gas stream to the gas plant, an output stream comprising aromatics to the aromatics separation unit, and a C₅/160 reformat stream to premium gasoline.

An alkylation unit is connected to receive a C₄ and lighter gas stream (butanes, butenes, and butylenes) from the butadiene recovery means and to receive butylenes and pentenes (light zeolite catalytic cracked gasoline—LT. ZEO. CAT. GASOLINE) from the catalytic cracking unit. The output streams from the C₄ and C₅ alkylation unit which comprise C₄ and C₅ alkylates, and C₆ with light catalytic cracked gasoline (LT. CAT. GAS) are routed to gasolines.

The aromatics extraction unit in this leaded gasoline version of the arrangement supplies a raffinate stream to regular gasoline and a stream containing benzene, toluene, and xylenes to the BTX Distillation unit. The BTX Distillation unit supplies (1) a benzene stream to the Benzene Hydrogenation unit in which cyclohexane is produced, (2) a toluene stream to the toluene dealkylation unit in which conversion to benzene takes place, and (3) a stream containing xylenes to the para xylene separation unit in which para-xylene is separated.

Part of the fuel gas generated in the gas plant is used, as previously described, by the hydrogen plant to produce hydrogen which is directed where needed to the refinery arrangement units such as the hydrotreater units, hydrocracker unit, toluene dealkylation unit, benzene hydrogenation unit, and para xylene separation units which require hydrogen.

The units which produce streams containing H₂S, such as the hydrotreater units, delayed coker unit, pyrolysis products separation unit and hydrocracker unit, supply these streams to an H₂S separation unit which sends an H₂S stream to the sulfur recovery unit in which elemental sulfur is recovered.

As shown in FIG. 1 the gasoline streams of the leaded gasoline version of the refinery arrangement are sent to anti-knock additive (A.K.A.) blending units where compounds such as tetraethyl lead are added to achieve the desired anti-knock rating.

The refinery arrangement may require, in addition to the crude oil inputs, additional amounts of isobutane and normal butane for use in the alkylation unit and for direct addition to the gasoline streams as shown in the drawings.

Another important aspect of the refinery arrangement of the invention involves the high degree of interaction between the hydrocracker unit and the other basic units. The hydrocracker unit, in the leaded gasoline version of the arrangement, receives as inputs, a gas oil fraction from the crude distillation unit, a gas oil fraction from the catalytic cracking unit, and a gas oil fraction from the ethylene and propylene producing means. The hydrocracker unit in this version of the arrangement supplies as outputs, C₄ fractions for the alkylation unit, heavy naphtha to the BTX reformer unit, light naphtha to gasolines, and heavy naphtha to the ethylene and propylene producing unit.

In shifting the material flows from the dashed lines to the dotted lines as shown in FIG. 1 to achieve a version of the refinery to produce suitable gasolines without lead additives, the following streams are modified:

(1) the C₅/160 light naphtha fraction directed from the crude distillation unit to regular gasoline is shifted instead to the pyrolysis unit of the ethylene and propylene producing plant,

(2) the C₅/160 reformat stream directed from the BTX reformer to premium gasoline is terminated,

(3) the C₆+LT. CAT. GAS stream directed from the alkylation unit to premium gasoline is terminated,

(4) the toluene stream directed from the BTX Distillation unit to the Toluene Dealkylation unit is shifted instead to premium gasoline,

(5) the C₅/160 thermal naphtha stream directed from the thermal naphtha hydrotreater to regular gasoline is shifted instead to the pyrolysis unit of the Ethylene and Propylene producing unit,

(6) the raffinate stream directed from the Aromatics Separation unit to regular gasoline is shifted instead to the Pyrolysis unit of the Ethylene and Propylene producing unit,

(7) the straight run gas oil streams and heavy naphtha stream directed from the Crude Distillation unit to the Hydrocracker unit and Pyrolysis unit of the Ethylene and Propylene Producing unit are reduced, terminating the straight run gas oil to the Hydrocracker unit entirely if desired, and a portion of these reduced straight run streams then combined as a No. 2 Fuel oil product as shown in dotted lines on FIG. 1.

Obviously, the anti-knock additives (A.K.A.) blending units are bypassed in this version of the refinery arrangement.

The relative capacities of the various units and relative sizes of the process streams are indicated by the numbers corresponding to each on the drawing which represent arbitrary volumetric units (A.V.U.) for the purpose of comparison. These relative capacities and sizes are predetermined and selected relative to each other, relative to a given range of possible crude oil feedstocks, and relative to a given slate of products such that the amounts of the products produced can represent an optimum in terms of total value and cost of producing them.

It is believed that the construction and operation of the refinery arrangement of this invention will be clear to those skilled in the art from the preceding description and discussions, considered with reference to the accompanying drawing. Further, it is believed to be apparent that an improved refinery arrangement has been provided in accordance with the objects of the invention.

The construction and operation of the individual component process units of the arrangement are conventional and well known to those skilled in the art and in addition are described in publications such as for example, the following:

(1) 1968 "Refining Processes Handbook," published in September 1968 issue of "Hydrocarbon Processing" magazine.

Although certain preferred embodiments of the invention have been described in detail in accordance with the patent law, many variations and modifications within the spirit of the invention will be obvious to those skilled in the art, and all such are considered to fall within the scope of the following claims.

What is claimed is:

1. A composite crude oil refinery arrangement for producing products comprising gasolines, ethylene, propylene, butadiene, aromatic hydrocarbons and coke, said arrangement comprising in combination; crude oil distillation means for separating a crude oil input product into a given number of fractions, catalytic hydrocracker means, alkylation means, catalytic cracking means, ethylene and propylene producing means comprising a steam cracking pyrolysis unit and a pyrolysis products separation unit, catalytic reforming means, and delayed coking means each of said latter four means operatively connected and cooperating with said crude oil distillation means, said arrangement further constructed, connected, and arranged such that said hydrocracker means receives certain input gas oil fractions (1) from said catalytic cracking means, and (2) from said ethylene and propylene producing means, and said arrangement further constructed, connected and arranged such that said hydrocracker means supplies certain outputs (1) comprising C_4 fractions for said alkylation means, (2) comprising heavy naphtha to said catalytic reforming means, (3) comprising light naphtha to gasoline fuel product streams, and (4) comprising heavy naphtha to said ethylene and propylene producing means, said delayed coking means operatively connected for receiving a pyrolysis tar fraction from said pyrolysis unit of said ethylene and propylene producing means, said delayed coking means further operatively connected for receiving a heavy cycle oil fraction from said catalytic cracking means and supplying a gas oil fraction to said catalytic cracking means and supplying a heavy naphtha fraction to said ethylene and propylene producing means, said arrangement further comprising an aromatic product recovery means operatively connected to receive, and separate aromatic products from, (1) naphtha reformat from said catalytic reforming means, and (2) pyrolysis naphtha from said pyrolysis unit of the ethylene and propylene producing means, the hydrocracker means having a capacity sufficient to handle streams of from about 10% to about 17% of the capacity of said crude oil distillation means, said delayed coker means having a capacity sufficient to handle streams of from about 13% to about 21% of the capacity of said crude oil distillation means, said catalytic cracking means having a capacity sufficient to handle streams of from about 33% to about 42% of the capacity of said crude oil distillation means, and said catalytic reforming means having a capacity of from about 22% to about 31% of the capacity of said crude oil distillation means.

2. A continuous process for operating a composite refinery arrangement to convert a crude petroleum oil to chemical products including olefins and aromatics and to fuel products including gasoline, said process comprising the following steps in combination; continuously separating by distillation a crude oil into a given number of fractions, catalytically cracking in a catalytic cracking zone, a gas oil fraction from said distillation separation step to form products comprising propane, a C_2 and lower gas fraction, gas oil and gasoline, thermally cracking in a thermal cracking zone, a residual heavy fraction

from said distillation separation step to form products comprising coke and a naphtha fraction, pyrolytically steam cracking, in a steam cracking zone, a gas oil fraction from said distillation separation step, naphtha from said thermal cracking step, and propane from said catalytic cracking step to form products comprising a heavy gas oil, tar fractions, ethylene, propylene, aromatic products, and butadiene, catalytically hydrocracking in a catalytic hydrocracking zone, a heavy gas oil from said pyrolytic steam cracking step and a gas oil from said catalytic cracking step to form products comprising a light gas oil and naphtha, supplying gas oil and naphtha from said catalytic hydrocracking step to said steam cracking zone to be used as additional inputs to said pyrolytic steam cracking step, supplying a residual tar fraction from said pyrolytic steam cracking step to said thermal cracking step zone to be used as additional inputs to said thermal cracking step, said catalytic cracking also cracking a gas oil fraction supplied by said thermally cracking and said thermally cracking also cracking a heavy cycle oil fraction supplied by said catalytic cracking, the relative volumes of the input fractions and streams to each of said zones selected and predetermined to produce from a given range of inputs to the distillation step a conversion of from about 25% to about 50% of the input to the distillation step to chemical products and a conversion of from about 50% to about 75% of the input step to the distillation step to fuel products.

3. The process of claim 2 in which the C_2 and lower gas fraction from the catalytic cracking step is added to the product stream from the pyrolytic steam cracking step.

4. The process of claim 2 in which a gas oil fraction from the distillation separation step is supplied to the catalytic hydrocracking zone as an input for the catalytic hydrocracking step.

5. The process of claim 2 in which naphthas from said distillation separation step, said catalytic hydrocracking step, and said thermal cracking step are catalytically reformed in a catalytic reforming zone to provide certain outputs comprising aromatic products and light naphtha reformat, the input fractions and streams handled in said catalytic hydrocracking zone being from about 10% to about 17% of the volume of the input stream handled by said distillation step, the input fractions and streams handled in said delayed coking step being from about 13% to about 21% of the volume of the input stream handled by said distillation step, the input fractions and streams handled in said catalytic cracking zone being from about 33% to about 42% of the volume of the input stream handled by said distillation step, and the input fractions and streams handled in said catalytic reforming zone being from about 22% to about 31% of the volume of said input stream handled by said distillation step.

6. The process of claim 5 in which the naphtha fraction supplied to the catalytic reforming zone from the distillation separation step and the naphtha supplied from the thermal cracking zone to the catalytic reforming zone are given a thermal catalytic hydrogenation treatment in a hydrotreating zone to remove products comprising sulfur from such naphtha fractions as hydrogen sulfide.

7. The process of claim 6 in which product streams from the catalytic hydrocracking zone, the thermal cracking zone, and from the hydrotreating zone are converted in a sulfur recovery zone to products including elemental sulfur and the elemental sulfur separated as a by-product.

8. A composite refinery arrangement for processing crude petroleum oil to convert crude oil to chemical products including olefins and aromatics and to fuels including gasoline, said arrangement consisting of, in combination; crude oil distillation means for separating input crude petroleum products into a given number of fractions, delayed coking means, catalytic cracking means, catalytic hydrocracker means and ethylene and propylene produc-

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ing means comprising a steam cracking pyrolysis unit and a pyrolysis products separation unit, said delayed coking means, catalytic cracking means and ethylene and propylene producing means operatively connected with and cooperating with said crude oil distillation means to receive certain fractions therefrom, said arrangement further consisting of aromatic product recovery means and butadiene recovery means each operatively connected with and cooperating with said separation unit of said ethylene and propylene producing means, said arrangement further constructed and arranged such that said pyrolysis unit receives (1) certain gas oil fractions from said distillation means, (2) certain naphtha and gas oil fractions produced by said hydrocracker means, and (3) certain naphtha fractions produced by said delayed coking means, the output of said pyrolysis unit being supplied to said pyrolysis products separation unit, said pyrolysis products separation unit of said ethylene and propylene producing means operatively connected to supply an output stream comprising benzene, toluene, and xylenes to said aromatic product recovery means, and an output stream comprising butadiene to said butadiene recovery means in addition to supplying product output streams of ethylene and propylene, said ethylene and propylene producing means further operatively connected to supply (1) by-products comprising heavy gas oil and pyrolysis tar fractions to said delayed coking means, and (2) by-products comprising gas oil fractions to said hydrocracker means, said delayed coking means operatively connected for receiving a heavy cycle oil fraction from said catalytic cracking means and supplying a gas oil fraction to said catalytic cracking means, the relative capacities of said means and the relative sizes of the streams handled by said means selected and predetermined to produce from a given range of petroleum input products a conversion of from about 25% to about 50% of the input products to chemical products and a conversion of from about 50% to about 75% of the input products to fuel products.

9. The arrangement of claim 8 in which said pyrolysis product separation unit of the ethylene and propylene producing means is operatively connected to receive propane and a C₂ and lower gas fraction from said catalytic cracking means.

10. The arrangement of claim 8 in which said hydrocracker means is operatively connected to receive an input stream comprising a gas oil fraction from said distillation means.

11. The arrangement of claim 8 which further consists of catalytic reforming means operatively connected with and cooperating with said distillation means, said hydrocracker means, and said delayed coking means to receive naphthas therefrom as inputs, said arrangement further consisting of alkylation means operatively connected to receive butenes and butanes from said butadiene recovery means and to receive butenes and pentenes from said catalytic cracking means; said catalytic reforming means, said hydrocracker means, and said alkylation means operatively connected and cooperating to combine certain of their output streams which comprise a light naphtha reformat fraction from the reforming means, a light naphtha fraction from said hydrocracker means, and C-4 and C-5 alkylates from said said alkylation means to produce gasoline fuel products.

12. The arrangement of claim 11 in which said crude oil distillation means is further constructed and arranged to produce a straight run fraction usable as jet fuel.

13. The arrangement of claim 12 which further consists of hydrotreater means connected (1) between the catalytic reforming means and the crude oil distillation means, to remove sulfur as hydrogen sulfide from the naphtha fraction moving from the crude oil distillation means to the reforming means, (2) between said delayed coker means and each of the catalytic reforming means and ethylene and propylene producing means to hydro-

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genate the unsaturated hydrocarbons and remove sulfur as hydrogen sulfide from the naphtha fraction moving from the delayed coker means to each of the reforming means and the ethylene and propylene means, and (3) between said pyrolysis products separation unit of the ethylene and propylene producing means and said aromatic product recovery means to hydrogenate the unsaturated hydrocarbons in the naphtha fraction moving from the pyrolysis products separation unit of the ethylene and propylene producing means.

14. The arrangement of claim 13 which further consists of sulfur recovery means operatively connected with said hydrotreater means, said hydrocracker means, said pyrolysis products separation unit, and said delayed coker means, for receiving streams containing hydrogen sulfide from the hydrotreater means, said hydrocracker means, and said delayed coker means, converting the hydrogen sulfide received to products comprising elemental sulfur, and separating elemental sulfur.

15. The arrangement of claim 14 which further consists of aromatic product separation means operatively connected with said aromatic product recovery means to receive therefrom an input stream containing benzene, toluene, and xylenes and separate such input stream to form individual streams of benzene, toluene, and xylenes.

16. The arrangement of claim 15 which further consists of para xylene separation means operatively connected with said aromatic product separation means to receive therefrom as an input stream the stream of xylenes and separate therefrom para xylene.

17. The arrangement of claim 16 which further consists of benzene hydrogenation means operatively connected with said aromatic product separation means to receive therefrom the benzene stream and convert it to cyclohexane.

18. The arrangement of claim 16 which further consists of toluene dealkylation means operatively connected with said aromatic product separation means to receive toluene therefrom and convert it to benzene and recycle the benzene to the aromatic product separation means.

19. The arrangement of claim 11 which further consists of gas separation means operatively connected with said distillation means, said delayed coking means, said catalytic reformer means, said ethylene and propylene producing means, said butadiene recovery means, said catalytic cracking means, said catalytic hydrocracker means, said toluene dealkylation means, and said para xylene separation means to receive therefrom C₄ and lighter gases, separate the same into certain component streams, and supply, in addition to fuel gas, propane to said ethylene and propylene producing means, mixed butenes and mixed butanes to said alkylation means, and a C₂ and lighter gas stream to the pyrolysis products separation unit of the ethylene and propylene producing means.

20. The arrangement of claim 19 which further consists of hydrogen producing means operatively connected to receive fuel gas from said gas separation means and convert the same to hydrogen for use in various means of said arrangement.

21. The arrangement of claim 11 which further consists of anti-knock additive blending means operatively connected to add anti-knock additives to gasolines produced by said arrangement.

22. The refinery arrangement of claim 8 wherein said hydrocracker means has a capacity of from about 10% to about 17% of the capacity of said crude oil distillation means, said delayed coking means has a capacity of from about 13% to about 21% of the capacity of said crude oil distillation means, and said catalytic cracking means has a capacity of from about 33% to about 42% of the capacity of said crude oil distillation means.

23. The refinery arrangement of claim 8 wherein said pyrolysis unit also receives propane from said catalytic cracking means.

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24. The refinery arrangement of claim 11 wherein said catalytic reforming means has a capacity of from about 22 to about 31% of the capacity of said crude oil distillation means.

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