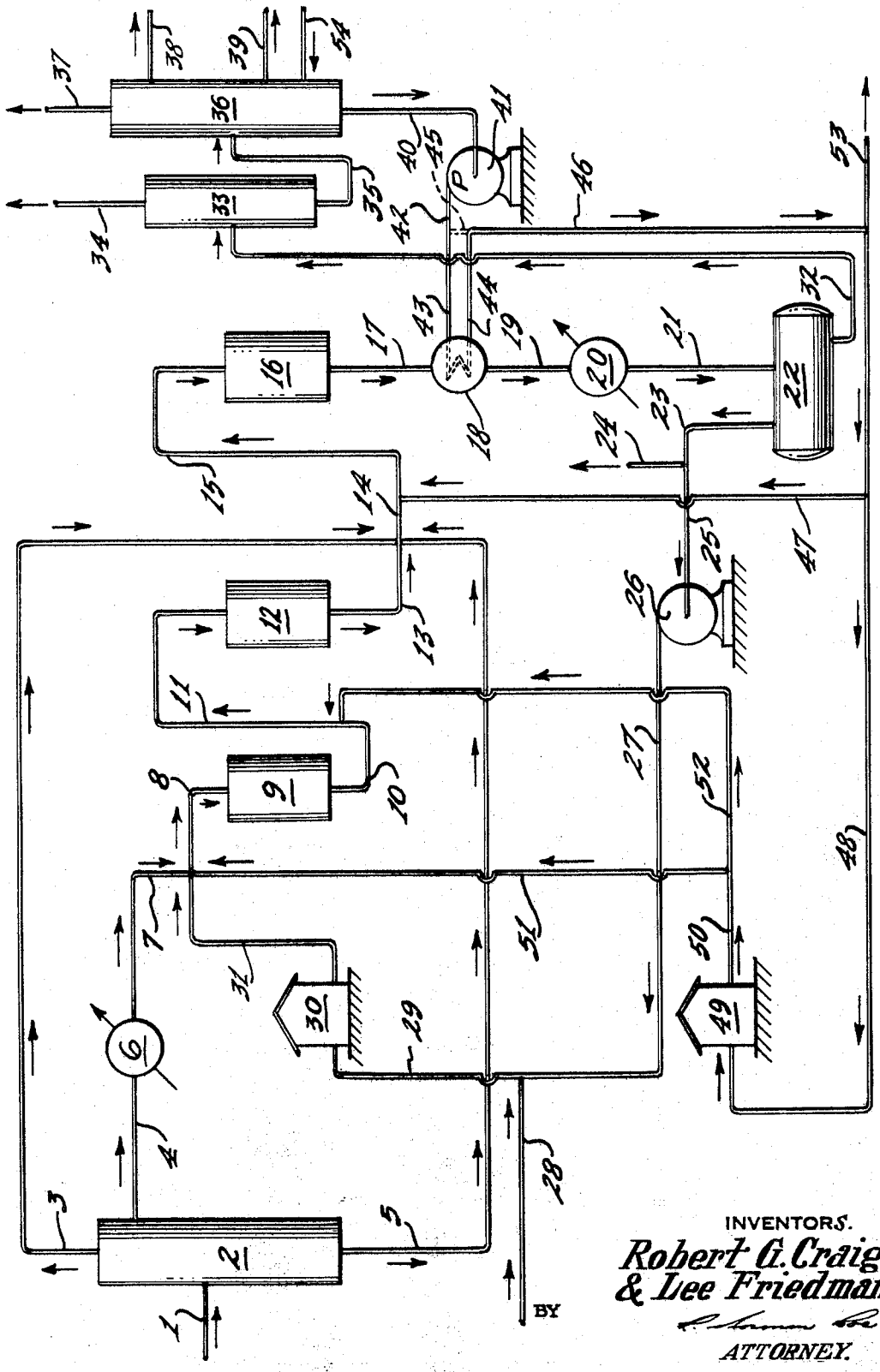
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CATALYTIC HYDROGENATION OF UNSATURATED HYDROCARBONS

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INVENTORS.
Robert G. Craig
& Lee Friedman

BY

ATTORNEY.

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CATALYTIC HYDROGENATION OF UNSATURATED HYDROCARBONS

Robert G. Craig, Fairfax, Wilmington, Del., and Lee Friedman, Bala Cynwyd, Pa., assignors to Air Products and Chemicals, Inc., Philadelphia, Pa., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

An unsaturated hydrocarbon distillate is fractionally distilled into three fractions. The middle fraction is catalytically hydrogenated in two reactors. The effluent from the second reactor is mixed with the light fraction and heavy fraction. The mixture is then catalytically hydrogenated in a third reactor and a wash oil is added to at least one reactor.

The present invention relates to the catalytic hydrogenation of unsaturated hydrocarbons having a high tendency to polymerize and more particularly, to the simultaneous partial and total hydrogenation of separate unsaturated hydrocarbon fractions for motor gasoline and aromatics production.

Unsaturated hydrocarbons boiling between about 75 to about 750° F. at atmospheric pressure, resulting from diverse conversion processes, including the catalytic and/or thermal cracking of petroleum, the destructive distillation of wood or coal, shale-oil retorting, etc., frequently contain sulfurous, nitrogenous and oxygenated compounds which render them unsuitable for most applications without further processing. In addition to the aforementioned contaminants, such hydrocarbons also contain appreciable quantities of styrene and other mono-olefins and di-olefins, the latter including compounds such as isoprene. An example of such unsaturated hydrocarbons is pyrolysis hydrocarbons, i.e., normally liquid hydrocarbons boiling in the range of 77 to 500° F., obtained as a by-product in the production of ethylene during the high temperature pyrolysis of gaseous and/or liquid hydrocarbons.

Suggestions directed to the selective hydrogenation of mono-olefins and/or di-olefins, without simultaneously hydrogenating aromatic compounds present in these unsaturated hydrocarbons, have generally been unsatisfactory due to such problems as comparatively low conversion rates, excessive coke make and catalyst deactivation. Especially troublesome is the presence of the di-olefins, which tend to form gum-like polymerization and co-polymerization products when heated to elevated temperatures of the order of 500 to 700° F. at which sulfur and nitrogen-bearing compounds are effectively hydrogenated to products which can be readily removed by known techniques.

In conventional operations directed to the hydrogenation of unsaturated hydrocarbons for motor gasoline production and aromatics production, it is necessary to cool, condense, fractionate and reheat between stages with only the aromatics extraction feed portion being processed in the final stage. This interstage processing is expensive because it substantially duplicates similar processing at the outlet of the final reaction stages.

In accordance with the present discovery, these difficulties are efficiently and economically overcome by the simultaneous partial hydrogenation and total hydrogenation of selected and distinct fractions of the unsaturated hydrocarbon charge. More specifically, in the present invention the raw unsaturated distillate to be processed is fractionated to give cuts of the boiling range desired in the finished product. The fraction to be produced completely free of mono-olefins and diolefins is then processed in a two reaction zone system in the normal manner. The fractions to be only partially hydrogenated are introduced into the system at the outlet of the second reaction zone and the combined fractions are then processed in a third reaction zone at the relatively mild conditions required for partial hydrogenation—the totally hydrogenated fraction from the second reactor serving to dampen the temperature rise effect in the third reactor. Products of the desired boiling ranges are then separated by fractionation.

The process of the present invention may be understood more clearly by reference to the accompanying drawing which is a schematic illustration of one particular embodiment. In the interest of simplicity and clarity, various heaters, condensers, compressors, valves, controls, instruments, etc., have been eliminated from the drawing. In explanation of the drawing, the hydrocarbon charge stock will be assumed to be a full boiling range hydrocarbon distillate having an initial boiling point of about 80° F., and an end boiling point of about 500° F. containing about 1000 p.p.m. each of combined sulfur and nitrogen.

Referring to the drawing, the hydrocarbon charge stock is initially introduced into the process flow through line 1, being separated in fractionator 2 to provide a light unsaturated gasoline fraction having an end boiling point of about 160° F. leaving via line 3; an unsaturated aromatics extraction feed fraction having a boiling point range of between about 160 to about 295° F., leaving via line 4; and a heavy unsaturated gasoline fraction having an initial boiling point of about 295° F., leaving via line 5. The fraction in line 4 is then passed through heat exchanger 6 and lines 7 and 8 into a first reaction zone 9 after being combined in line 8 with a hydrogen-rich gas stream from line 31 and a gas oil distillate having a boiling point within the range of from 450 to 700° F., designated herein as wash oil from line 51.

Hydrogen purity in the hydrogen-rich gas stream is not critical and can be between 30 to 100% but it is preferred that the hydrogen-rich gas stream contain between 50 to 100% hydrogen. The rate of addition of this hydrogen-rich gas stream can be between 1500 and 10,000 s.c.f./bbl. or higher with preferred addition being in the range of 3,000 to 7,000 s.c.f./bbl. Admixture of wash oil with the material charged to the first reaction zone helps to insure against the formation of polymerization products or deposition on the catalyst and also to control the temperature rise across the catalyst in the reaction zone. Such admixture of wash oil with the unsaturated aromatics extraction feed fraction should take place as close to the point of contact between the admixture and the catalyst as feasible to obtain proper mixing while providing as little time as possible for promoting thermal polymerization. The temperature of the total charge to the first reacton zone is about 450° F. Operating conditions for the reaction zone itself include a temperature within the range of about 450 to about 550° F. and a pressure within the range of about 200 to about 1200 p.s.i.g.

The partially hydrogenated effluent from the first reaction zone 9, at a temperature of about 500 to 550° F., passes through line 10 and after admixture with additional wash oil from line 52 passes through line 11 into the second reaction zone 12 which it enters at a temperature of about 600° F. An elevated temperature of between 600 to about 700° F. is maintained in the second reaction zone 12 to complete the saturation of the mono-olefinic hydrocarbons and to convert nitrogenous and sulfurous compounds into ammonia, hydrogen sulfide and hydrocarbons.

The total liquid product from the second reaction zone,

at a temperature of about 650 to about 700° F., is passed through line 13 and combined with hydrocarbon fractions from lines 3 and 5. The combined fractions in line 14 are then cooled with additional wash oil from line 47 and introduced via line 15 at a temperature of about 450° F. into a third reaction zone 16. Mild conditions in this third reaction zone, including temperatures between about 450 to about 550° F., are maintained to effect only partial hydrogenation of the unsaturated materials present in the feed introduced into this final reactor. As previously indicated, the totally hydrogenated effluent from the second reaction zone, together with the added wash oil, serves to dampen any temperature rise effects in this third reaction zone.

The effluent from the third reaction zone is passed via lines 17 and 19 through one or more heat exchangers 18 and 20 prior to being passed through line 21 into high pressure separator 22. Separator 22 operates under essentially the identical pressure as reaction zone 16 and in effect controls the operating pressure of 200 to 1200 p.s.i.g. and preferably 400 to 800 p.s.i.g. maintained within each of the reaction zones. In fact, the operating pressure within separator 22 may be employed as an indication of the quantity of make-up hydrogen which must be added to the process via line 28. Separator 22 operates at essentially ambient temperatures of the order of 100° F. or less and serves to separate the total product effluent from reaction zone 16 into a gaseous phase and a normally liquid hydrocarbon phase.

The gaseous phase, substantially rich in hydrogen but also containing ammonia and hydrogen sulfide as well as light paraffinic hydrocarbons, such as methane, ethane and propane introduced with the make-up gas, is withdrawn from the separator via line 23 and is passed to compressor 26 via line 25. Compressed gas is then discharged into line 27 and after subsequent purification and/or admixture with make-up hydrogen supplied from line 28 is passed through line 29, heater 30 and line 31 where it is then admixed with the fraction in line 7. At least a portion of the gaseous phase in line 23 is withdrawn or vented from the system via line 24 for the purpose of preventing any undue buildup ammonia and hydrogen sulfide in the system.

The normally liquid product effluent from separator 22 is removed via line 32 and is passed to a standard final separation zone comprising a stabilizer 33 and a fractionator 36. Light gases are removed from the stabilizer via 34 while the remaining liquid hydrocarbons are passed via line 35 to fractionator 36. At least three fractions are recovered from the fractionator, viz., a light gasoline fraction, via line 37; an aromatics fraction (normally, benzene, toluene and xylene), via line 38, which may be passed to a further separation or recovery operation (not shown); and a heavy gasoline fraction, via line 39. Bottom material in the fractionator is recycled as wash oil and facilitates in the control of the various temperature and flow rates within the process.

Thus, the wash oil is removed from fractionator 36 via line 40, passed through pump 41 and transmitted into line 42. Preferably, this wash oil is sent via lines 43 and 44 through heat exchanger 18 where it is employed to cool the effluent from the third reaction zone. Optionally however, the entire wash oil or a fraction thereof may be passed through line 45 into line 46 for a recycle back into the system. As previously described, the wash oil in line 46 may be passed through line 47 to effect temperature control in the third reaction zone and also through lines 48 and 50 to 52 for control of the reaction in the first and second reaction zones. Tempreature of the wash oil supplied to the first and second reaction zones is controlled by heater 49.

Periodically, it is desirable to purge a small amount of wash oil from the system. This may be accomplished via line 53. Make-up wash oil, such as No. 2 furnace oil or any other suitable gas oil distillate boiling within the range of 450 to 700° F., may be added to the system via line 54.

Various modifications may be made to the illustrated embodiment by those possessing the requisite skill within the art of petroleum processing which do not remove the resulting process from the broad scope and spirit of the present invention as set forth in the appended claims. For example, separator 22 may be combined with additional separating and/or adsorbing means such as water injection means for adsorbing ammonia from lines 23 and/or 24. Similarly, the gaseous phase from separator 22 may be so treated as to effect substantially complete removal of hydrogen sulfide and/or light paraffinic hydrocarbons. Also, through the use of a suitable wash oil recycle storage vessel, the rate of wash oil recycled to each of the reaction zones may be controlled. In addition, hydrogen-rich gas may be separately introduced into lines 11 and/or 15 in addition to the hydrogen-rich gas supplied to the system in line 31. Water or any other cooling media may be employed to effect heat exchange of any feed or product line. Likewise, steam or any other suitable heating media may be utilized in the heat exchange system for increasing the temperature of feed or product streams.

In some instances, it may be desirable to provide for multi-point introduction of the reaction charge at various sections of the reaction zones in order to maintain a desired heat balance in said zones. For temperature control in the reaction zones, it may also be desirable to provide for alternate injection points for the wash oil. While the process of the present invention is most advantageously effected in three reaction zones, additional reactors could be employed or one or more of the reaction zones can be located within the same housing.

Reaction space velocity in the reaction zones is within the range of about 0.5 to about 10.0 or more LHSV with preferred space velocities between 1 and 4 LHSV (liquid hourly space velocity). Space velocity is correlated with reaction temperature and pressure to obtain the desired degree of saturation in each reaction zone. In general, as the reaction temperature increases, the space velocity also increases.

The quantity of wash oil which is recycled and combined with the charge to the reaction zones is preferably such that the combined feed ratio to each of said zones lies within the range of from about 0.5:1 to about 6:1 and preferably from about 0.5:1 to about 2:1.

The catalyst employed in each of the reaction zones may have the same or different chemical and physical characteristics. Preferred catalysts are disclosed in U.S. Letters Patent No. 2,880,171 and 2,993,868. Generally, suitable catalytic composities for utilization in the present process will comprise metallic components selected from the group consisting of Groups VI–A and VIII of the Periodic Table and compounds thereof. A particularly suitable hydrogenation catalyst is nickel supported on a suitable base such as silica, alumina, calcium carbonate, or any other base or mixture of one or more bases which has a low activity for cracking and polymerization reactions. Other desired metallic components include chromium, molybdenum, tungsten, iron, cobalt, ruthenium, platinum, palladium and mixtures of two or more of these components with or without nickel.

When the foregoing conditions of operation and processing techniques are followed, the process of the present invention is capable of effecting efficient simultaneous partial and total hydrogenation of a full range, unsaturated hydrocarbon distillate, over extended periods of time. The tendency of high molecular weight polymer and co-polymer formation as well as a tendency for the formation of inhibitive amounts of coke and other carbonaceous materials is overcome so completely that the catalyst in the reaction zone is active for substantial periods. However, as with virtually all catalytic conducted processes, there is a slow but naturally-occurring deactivation of the catalyst

during operation. After three to six months, when coke on the catalyst reaches a level such that the catalyst activity is inadequate to promote the desired reaction, the catalyst may readily be reactivated in situ in known manner.

The invention is further clarified by reference to the following examples.

Example I

In accordance with this example, the simultaneous treatment of pyrolysis gasoline (C_5 to 400° F.) is provided wherein the BTX (benzene, toluene, xylene) fraction of the raw feed is hydrogenated to the following specification:

Bromine number	<1
Diene content	Nil
Sulfur	<1 p.p.m.
Nitrogen	< 1p.p.m.

and fractions other than BTX are partially hydrogenated to provide cuts, essentially free of gum-forming tendencies, suitable for blending into motor gasoline.

The catalyst composite within each of the three reaction zones is composed of 0.2% nickel, 1.7% cobalt and 9.5% molybdenum deposited on an alumina support. This catalyst composite is prepared by first calcining the alumina base at an elevated temperature of about 1100° F. Molybdenum is then deposited on the calcined base from a solution prepared by dissolving ammonia paramolybdate in ammonical water solution. After drying, the material is calcined at 900° F. for about 10 hours. The cobalt and nickel metals are deposited upon the molybdenum-alumina material from a water solution of the metal nitrates. After drying, the material is again calcined at a temperature of about 900° F. for about 10 hours.

The raw charge stock is initially fractionated to provide a light unsaturated gasoline fraction having an end boiling point of about 160° F., an unsaturated aromatics fraction having a boiling point range of between about 160 to about 295° F. and a heavy unsaturated gasoline fraction having an initial boiling point of about 295° F. For convenience, these fractions will be referred to hereinafter as the C_5 fraction, the BTX fraction and the C_9^+ fraction, respectively.

The BTX fraction is blended with previously recycled wash oil in a combined feed ratio of about 2:1 and about 1500 s.c.f./b.b.l. of hydrogen-rich gas. This mixture enters the first reaction zone at an inlet temperature of about 450° F. Reactor effluent from the first reaction zone having a temperature within the range of 500 to 550° F. is then admixed with additional wash oil in a combined feed ratio of about 1.2:1. This admixture is then introduced into the second reaction zone at an inlet temperature of 600° F. The C_5 and C_9^+ fractions are blended with the second reaction zone effluent, combined with additional wash oil recycle in an amount to result in a combined feed ratio of about 1.2:1 and introduced at about 450° F. into a third reaction zone. Pressure in each reaction zone is maintained at about 800 p.s.i.g. and the space rate for each reactor is 2 LHSV based on the combined feed and wash oil. The effluent product from the third reaction zone is then cooled to a temperature of about 100° F. and passed to a high pressure separator.

A portion of the gaseous hydrogen-rich stream obtained from the separator is vented, while the remaining portion is recycled and combined with make-up hydrogen for addition to the liquid charge to the first reaction zone. The normally liquid product effluent, following separation in the high pressure separator, is passed to a conventional stabilizer and then fractionated to obtain at least a light gasoline product (C_5 product), an aromatics product (BTX fraction) and a heavy gasoline product (C_9^+ product). Remaining material is recycle as wash oil for admixture with the charge to each of the three reaction zones.

The overall material balance (excluding recycle wash oil) for this operation is shown in the following table. Amounts are given in pounds per hour.

	Fresh Feed	Make-up Gas	Vent Gases	Stab. Off-Gas	C_5 Product	Aromatics to Extraction	C_9^+ Product
H_2		160	43	1			
C_1		157	114	43			
C_2		154	45	109			
C_3		128	13	115			
C_4		81	3	58	20		
C_5	260	58	10	180	1,242	100	
$C_5^=$	407		19	80	598	177	
C_5^-	1,918						
C_6^- and Sat.	488		3	8	9	479	
B	2,031		8	8	38	1,977	
T	2,229		4			2,225	
X	1,041					1,190	106
Styrene	250						
$C_9^=$	125						
C_9^-	251						235
C_9^+	3,532					231	3,779
Total	12,532	738	262	602	1,907	6,379	4,120

It can be seen that the BTX fraction is processed for complete hydrogenation of olefins and diolefins while the C_5 and C_9^+ fractions are simultaneously processed in accordance with the present invention for hydrogenation of cyclo- and di-olefins. Mono-olefins are retained in these latter fractions since they do not significantly contribute to the formation of gums in gasoline and they have a desirable octane rating.

Example II

The feedstock employed in this example had the following composition.

Components:	Wt. percent	
C_5 saturates	2.2	
C_5 olefin	2.0	
C_6 diolefin	4.3	
Isoprene	3.2	
Cyclopentadiene	6.5	
		18.2
C_6 saturates	0.9	
Benzene	30.0	
Methyl cyclopentane	1.1	
C_7 saturates	2.2	
Toluene	23.0	
Xylene	15.0	
Ethylbenzene	4.0	
C_9 saturates	2.2	
C_9 aromatics	1.1	
C_{10} aromatics	2.2	
C_{11} aromatics	0.1	
		81.8
Total C_6^+		100.0

This feedstock is processed substantially according to Example I with the exception that in the final product fractionation step only two products (C_5 product and an aromatic stream) are recovered. It is to be understood, however, that the product aromatic stream may be subjected to additional and subsequent treatment to effect the separation of the BTX materials and the C_9^+ materials.

The overall material balance, (excluding recycle wash oil) for this operation is shown in the following table. Amounts are given in the table as pounds per hour.

	Raw Feed	Make-Up Gas	H_2 Purf. Reject	Vent Gases	Stab. Off-Gas	C_5 Product	Aromatics to Separation
H_2		320	12	46	5		
C_1		1,379	1,105	104	170		
C_5-Sat.	1,613			18	50	2,498	108
C_5	977			7	20	4,649	210
C_5=	4,740					4	
C_6^+ Sat.	2,591			14	8	43	2,526
B	14,660			10	6	30	14,614
T	11,239						11,239
X	8,063						9,308
Styrene	1,222						
C_9^+ Arom.	3,758						3,758
Total	48,863	1,699	1,117	199	259	7,224	41,763

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. A process for the simultaneous partial and total hydrogenation of selected distinct fractions of unsaturated hydrocarbon distillate which comprises initially fractionating said distillate to provide a light fraction having an end boiling point of about 160° F., an unsaturated fraction having a boiling point range of about 160 to 295° F. and a heavy fraction having an initial boiling point above about 295° F.; reacting said unsaturated fraction with hydrogen in a first reaction zone at a temperature of about 450 to about 550° F.; reacting the effluent from the first reaction zone in a second reaction zone at a temperature of about 600 to about 700° F.; combining the reaction effluent from the second reaction zone with the light fraction and the heavy fraction; reacting the resulting combined mixture in a third reaction zone at a temperature of about 450° F. to about 550° F. and separating the effluent from said third reaction zone into a gaseous product and a liquid product, in which process wash oil boiling within the range of about 450 to 700° F. is admixed with the material charged to at least one of the aforementioned reaction zones, said process being further characterized in that said first, second and third reaction zones have disposed therein a catalyst composite of at least one metallic component selected from the group consisting of VI–A and VIII of the Periodic Table and the reaction space velocity in the reaction zones is within the range of about 0.5 to about 10.0 LHSV.

2. The process of claim 1 wherein the wash oil is admixed with material charged to at least one of the reaction zones in an amount to result in a combined feed ratio to the reaction zone of about 0.5:1 to about 6:1.

3. The process of claim 1 wherein the catalyst composite comprises molybdenum and at least one metallic component from the metals of the iron group of the Periodic Table.

4. The process of claim 1 wherein the reaction space velocity in the reaction zones is between about 1 and 4 LHSV.

5. The process of claim 1 further characterized in that the pressure in the reaction zones is between about 200 and 1200 p.s.i.g.

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HERBERT LEVINE, *Primary Examiner.*