

APPARATUS AND PROCESS FOR HYDROGENATIONS

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to an apparatus and process for improving the flexibility of operation of reactive distillation hydrogenation processes.

Related Art

10 The use of catalysts in a distillation column to concurrently carry out chemical reactions and separate the reaction products has been practiced for some time. Surprisingly, this use of a catalytic distillation column reactor lends itself particularly well for hydrogenations. See for example, U.S. Patents 5,595,634; 5,599,997; 5,628,880; 5,773,670 and European Patent No. 0556025 B1.

15 The combination is useful because the reactants in the liquid phase are quickly separated from the reaction products due to boiling point differences by fractional distillation. Thus further reaction is suppressed.

20 Several different arrangements have been disclosed to achieve the desired result. For example, British Patents 2,096,603 and 2,096,604 disclose placing the catalyst on conventional trays within a distillation column. A series of U.S. patents, including those listed above and more, particularly U.S. Patents 4,443,559 and 4,215,011 disclose

25 using the catalyst as part of the packing in a packed distillation column. The use of multiple beds in a reaction distillation tower is also known and illustrated, for example, in U.S. Patents 4,950,834; 5,321,163; and 5,595,634.

30 In reactive distillations, such as catalytic distillation, as in any other distillation, there is no rigid cut off between the components. Reactions carried on in specified portions of the column using some constituents may leave undone other desirable treatment of

35 other portions of the column constituents.

For example, mixed refinery streams often contain a broad spectrum of olefinic compounds. This is especially true of products from either catalytic cracking or thermal

cracking processes (pyrolysis gas). These unsaturated compounds comprise ethylene, acetylene, propylene, propadiene, methyl acetylene, butenes, butadiene, amylenes, hexenes, etc. Many of these compounds are valuable especially as feed stocks for chemical products. Olefins having more than one double bond and the acetylenic compounds (having a triple bond) have lesser uses and are detrimental to many of the chemical processes in which the single double bond compounds are used, for example, polymerization. Sulfur and nitrogen compounds, among others, are frequently desirably removed also and they may be effectively removed from a portion of the column constituents, but because of different boiling points for other portions of the column constituents and the contaminants therein, not all of the contaminants may be removed.

Generally it is more difficult to remove both dienes and olefins than dienes alone. Diene-rich streams will hydrogenate at a higher volumetric rate under milder conditions than will a diene depleted olefinic stream. Sulfur in the several hundred ppm range is not uncommon for some feeds. Palladium hydrogenation catalysts are not able to handle such high sulfur levels, however, double-digit diene levels often present in these feeds overwhelm the sulfur impurities in their mutual competition for catalyst sites thereby providing reasonable rates notwithstanding.

In hydrotreating streams with high concentrations of dienes present (above 1000 ppm), there is a need to refrain from using high temperatures to avoid oligomerization. Generally, temperatures in the area of 170°F or above are avoided. Such operating restraints create conditions which are unfavorable for exhaustive olefin conversion in the same unit in which the diene is eliminated.

The present invention provides apparatus and process to address the reactive distillation hydrogenation of feed streams having concentrations of both mono and di-olefins.

SUMMARY OF THE INVENTION

The present invention includes an apparatus for conducting reactive distillations comprising a first distillation column, a first primary catalyst bed for carrying out a hydrogenation of unsaturated compounds comprising diolefins, said first primary catalyst bed being positioned in said distillation column to provide a first reaction zone for diolefins in said first distillation column, and optionally, a first secondary catalyst bed above said first primary catalyst bed, said first secondary catalyst bed to provide a second reaction zone for diolefins remaining in said first distillation column after said first reaction zone, a first mixed saturated/unsaturated compound feed entry below said first primary bed, a hydrogen feed below said primary bed, a bottoms line and an overhead line connecting to a second distillation column comprising a second primary catalyst bed for carrying out hydrogenation of unsaturated compounds comprising mono olefins from said first distillation column, said second primary catalyst bed being positioned in said distillation column to provide a first reaction zone for unsaturated compounds in said second distillation column, and optionally, a second secondary catalyst bed below said second primary bed, said second secondary catalyst bed to provide a second reaction zone for mono olefins remaining in the second distillation column after said first reaction zone, said overhead line from said first distillation column connecting to said second distillation column above said second primary catalyst bed and a hydrogen feed below said second primary bed.

The process carried out in the apparatus is also part of the present invention.

There may be distillation structures or trays between the primary and secondary beds. Hydrogenation reactions liberate a significant heat of reaction (on the order of 50,000 or greater BTU/lb mole H_2 consumed). This released heat adds to vapor load in the column. Optionally, side condensers may be used to keep the uniformity of the vapor

profile in the column within desired ranges.

A secondary catalyst bed may be positioned in the distillation column, above or below the primary bed as heretofore described, to allow lighter or heavier boiling components to be exposed to additional catalyst and be purified or treated further.

The term "reactive distillation" is used to describe the concurrent reaction and fractionation in a column. For the purposes of the present invention, the term "catalytic distillation" includes reactive distillation and any other process of concurrent reaction and fractional distillation in a column regardless of the designation applied thereto.

The catalyst beds as used in the present invention may be described as fixed, meaning positioned in a fixed area of the column and include expanded beds and ebulating beds of catalysts. The catalysts in the beds may all be the same or different so long as they carry out the function of hydrogenation as described. Catalysts prepared as distillation structures are particularly useful in the present invention.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a simplified process flow diagram of one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is particularly useful for removal of mono olefins and diolefins from cracked gas streams. Thermally cracked gas streams have a particularly wide range of carbon numbers and compound types. Normally, compounds in one carbon number range (such as C₄'s in a C₄/C₅ splitter) will function as the light key grouping in the column. Thus compounds one carbon number greater (such as C₅'s in a C₄/C₅ splitter) will serve as the heavy key grouping for the column.

Hydrogenation is the reaction of hydrogen with a carbon-carbon multiple bond to "saturate" or partially saturate the compound. This reaction has long been known and is usually done at super atmospheric pressures and moderate temperatures using a large excess of hydrogen over a metal

catalyst. Among the metals known to catalyze the hydrogenation reaction are platinum, rhenium, cobalt, molybdenum, nickel, tungsten and palladium. Generally, commercial forms of catalysts use supported oxides of these metals. The oxide is reduced to the active form either prior to use with a reducing agent or during use by the hydrogen in the feed. These metals also catalyze other reactions, most notably dehydrogenation at elevated temperatures. Additionally, they can promote the reaction of olefinic compounds with themselves or other olefins to produce dimers or oligomers as residence time is increased.

Selective hydrogenation of hydrocarbon compounds has been known for quite some time. Peterson et al in "The Selective Hydrogenation of Pyrolysis Gasoline," presented to the Petroleum Division of the American Chemical Society in September of 1962, discusses the selective hydrogenation of C₄ and higher diolefins. Boitiaux et al in "Newest Hydrogenation Catalyst", Hydrocarbon Processing, March 1985, presents a general overview of various uses of hydrogenation catalysts.

FIRST COLUMN

The first column is operated with the catalyst located above the hydrocarbon feed. It is operated under conditions to reduce only dienes by hydrogenation. The column is operated to move a key component, for example C₅, upward into the primary and any secondary beds under conditions of pressure and temperature to hydrogenate only the dienes, e.g., 150°F to a top temperature of 170-200°F at 10 to 75 psig. The exact upper temperature will depend on the diene makeup and other unsaturates such as the acetylenes and the stability of the particular mix of unsaturates to oligomerization.

The upflow of the key component operates the paradigm shift that keeps the catalyst clean and inhibits coking of the dienes. The faster reaction rates of the dienes compared to the mono olefins in hydrogenation allow short superficial vapor phase contact times in the range of 20-60

seconds.

The heaviest carbon-range number that is directed upward serves as the light-key carbon range for the column. Compounds of lower carbon number than this behave as the "lighter than light keys" of the system. These lighter compounds tend to equilibrate more into vapor than into liquid which makes reaction for the dienes in that carbon group much more difficult. However, use of a secondary reaction zone with catalyst (above at a lower temperature than the primary bed) allows the concentration of this lower carbon number fraction. Thus, the combined primary bed and the optional upper secondary bed together handle a wider boiling range than would otherwise be achievable.

SECOND COLUMN

The second column revives the diene depleted overhead from the first column and feeds it above the primary and any optional secondary beds where it is hydrogenated in the reactive distillation mode. In the near absence of dienes e.g. <0.1 wt%, higher temperatures in the range of 200-325°F are used at pressures in the range of 60-150 psig. Mono olefins-only systems tend to have less favorable hydrogen uptake than diene-rich streams. The superficial vapor phase contact time even under the more severe conditions is 50-90 second range. Note that the key component carbon numbers in the second column may be coincident with or separate from the key component carbon numbers in the first column depending on the objectives of the operation.

The key component builds up in the column liquid and favors the reaction on the key component. In contrast the heavier carbon-range fraction thins out in the downflowing liquid. However, inclusion of a bottoms secondary catalyst bed (which is lower in the column where the higher temperature causes more boil up of the heavies) can be used to concentrate the heaviest carbon-number range species and react the heavier olefins out more effectively also. As in any distillation there is a temperature gradient within the distillation column reactor. The temperature at the lower

end of the column contains higher boiling material and thus is at a higher temperature than the upper end of the column.

5 The result of the operation of the process in the distillation column reactor is that lower hydrogen partial pressures (and thus lower total pressures) may be used.

10 It is believed that the present distillation column reaction is a benefit first, because the reaction is occurring concurrently with distillation and the initial reaction products and other stream components are removed from the reaction zone(s) as quickly as possible reducing the likelihood of side reactions. Second, because all the components are boiling, the temperature of reaction is controlled by the boiling point of the mixture at the
15 system pressure. The heat of reaction simply creates more boil up, but no increase in temperature at a given pressure. As a result, a great deal of control over the rate of reaction and distribution of products can be achieved by regulating the system pressure. A further
20 benefit that this reaction may gain from distillation column reactions is the washing effect, particularly in the downflow operation of the second column that the internal reflux provides to the catalyst thereby reducing polymer build up and coking.

25 Referring now to the figure, a process flow diagram for the removal of unsaturates, primarily mono- and di-olefins from a full range pyrolysis gas. Such items as reboilers, compressors, pumps and the like have been omitted but their normal utilization is readily apparent to those in
30 the art.

The feed, a pyrolysis gas as described in TABLE 1, enters the first column 10 via line 12.

TABLE 1

	Component	Wt %
	BD/C4Acetylene	0.2
	Butylenes	0.1
5	Butanes	0.0
	C5 Saturates	1.0
	C5 Olefins	4.2
	C5 Diolefins	13.0
10	C6 Saturates	2.7
	C6 Olefins	2.3
	C6 Diolefins	7.0
	C7 Saturates	1.5
	C7 Olefins	1.1
	C7 Diolefins	3.4
15	C8 Saturates	0.5
	C8 Olefins	0.4
	C8 Diolefins	1.2
	Benzene	18.7
	Toluene	17.4
20	EthylBenzene	2.1
	Xylenes	7.6
	Styrene	2.6
	Heavier	12.9
25	Total	100.0

In this illustration the tower 10 is operated under conditions to take the C₆ fraction upward (bottoms -394°F top -212°F at 60 psig.) The C₇ and heavier carbon atom components are removed via line 34 for other processing. The C₆ fraction contains some C₇ and heavier but is comprised of predominantly C₆ and lighter carbon number components.

C₆ components contain principally alkanes, benzene, 5 to 12% mono olefins and 15 to 35% dienes. Similarly, the lighter components contain a wide distribution of species including dienes and mono olefins. Hydrogen is added via line 14 at a rate to provide an excess stoichiometric amount to the dienes present in the C₆ and higher fraction. In bed 16 a hydrogenation catalyst is provided in the form of distillation structure. Under the conditions of temperature and pressure described there is both a vapor and liquid phase comprised principally of the C₆ components and as a result the C₆ dienes are substantially eliminated.

The higher components under these conditions are principally vaporous in bed 16. However, the temperature in bed 18, also a hydrogenation catalyst as a distillation

structure, is lower because of temperature gradient in the column. The secondary bed 18 allows the lower boiling components to undergo the same type of two phase contact as the C_6 fraction in bed 16 thereby allowing a concentration of this higher portion with the dienes substantially eliminated. A side draw 44 is used to remove a portion of the lights diene-depleted concentrate and diene-depleted C_6 into collector 40. A portion of the collected material can be returned via line 42 (dotted line) to the column 10 to maintain the vapor load on the column. Otherwise the material from side draw 44 is fed to the second column 48 via line 46.

An overhead 20 also containing mostly diene-depleted C_5 , C_6 and lighter material goes through condenser 22 into collector 24. The non-condensibles are removed for recycle to the hydrogen feed 14 or for disposal via line 26. A portion of the condensed material is returned as reflux 36 to column 10 and the remainder fed via 38 to line 46 into column 48.

The feed from column 10 is characterized as having almost all of the diene and greater unsaturates (acetylenes) removed by hydrogenation with little formation of oligomers. The olefins are substantially untouched because of the restricted operating temperature.

In column 48 the operating conditions are more severe in order to hydrogenate the mono olefins (bottoms -338°F , top -251°F at 100 psig). The feed enters above primary catalyst bed 50 which is a hydrogenation catalyst prepared as a distillation structure. Again, the conditions are such that the key component, the C_6 constituents, is moved downward. The lighter components, primarily C_5+ , exit via overhead line 54 through condenser 52 into collector 58. The non-condensibles are removed either for disposal via line 56 or recycle via line 60 to hydrogen feed 62. A small portion of the liquid in collector 58 is removed via line 78 and the remainder returned via line 76 to column 48 as reflux.

A collector 66 is located on side draw 64 which removes

hydrogenated product via line 74. A portion may be returned via line 68 to control the vapor load on the column. Alternatively the side draw stream 64 may be recovered as a vapor (elimination of the collector 66), which, although it will result in an energy penalty, will provide other benefits, namely (a) further retention of the heavy olefins in the secondary bed 72 and (b) a greater increase in the temperature of bed 72 relative to the primary bed 50, both of which enhance the performance of the secondary bed.

Secondary bed 72 contains a hydrogenation catalyst as a distillation structure and any heavier fraction remaining is concentrated and given a polishing hydrogenation and recovered via line 70 for combination with the side draw stream 74 into product stream 80.

Table 2 shows the temperature profile and distribution of the materials in the column 10. The conditions in the secondary catalyst bed 18 (corresponds to trays 4-16) and the primary bed 16 (corresponds to trays 17-30) are represented by the blocked out areas. The other trays are denoted by number. Tray 48 is the reboiler.

TABLE 2

	TRAY	TEMP °F	PRESSURE PSIA	LIQUID LBM/H	VAPOR LBM/H	FEED LBM/H	PRODUCT LBM/H
5	1C	101.4	74.7	3510			290.6 vap. 140.2 liq.
	2	211.6	74.7	4912	3940		
	3	215.8		4902	5343		
10	BED	217.7	75.1	4851	5332		
	18	219.5	75.3	4794	5282		
		221.3	75.5	4730	5225		
		223.3	75.7	4658	5161		
		225.6	75.9	4577	5089		
15		228.4	76.1	4485	5008		
		231.9	76.3	4385	4916		
		236.0	76.5	4278	4815		
		240.6	76.7	4170	4709		
		245.7	76.9	4064	4601		
20		250.8	77.1	3962	4495		
		255.9	77.3	3863	4392		
		260.8	77.5	3266	4294		503.8 Liq
25	BED	265.6	77.7	3184	4201		
	16	269.4	77.9	3113	4118		
		272.4	78.1	3050	4047		
		274.6	78.3	2995	3985		
		276.2	78.5	2945	3930		
		277.3	78.7	2898	3879		
30		278.1	78.9	2852	3832		
		278.7	79.1	2808	3787		
		279.2	79.3	2764	3743		
		279.7	79.5	2719	3698		
		280.2	79.7	2672	3653		
35		281.0	79.9	2621	3606		
		282.2	80.1	2563	3555		
		284.3	80.3	2489	3497		
40	31	288.1	80.5	2376	3423		
	32	296.2	80.7	3532	3311	1206.2 liq. 237.0 vap.	
	33	310.2	80.9	3645	3023		
	34	315.3	81.1	3648	3136		
	35	319.7	81.3	3645	3139		
45	36	324.1	81.5	3639	3136		
	37	328.7	81.7	3632	3131		
	38	333.6	81.9	3626	3124		
	39	338.7	82.1	3621	3117		
	40	343.8	82.3	3618	3112		
50	41	348.7	82.5	3616	3110		
	42	353.2	82.7	3613	3108		
	43	357.5	82.9	3608	3105		
	44	361.6	83.1	3597	3099		
	45	366.1	83.3	3575	3088		
	46	371.6	83.5	3532	3066		
55	47	379.8	83.7	3450	3023		
	48R	393.5	83.9		2941		508.7 liq.

Table 3 shows the temperature profile and distribution of materials in column 48. The conditions in the secondary catalyst bed 72 (corresponds to trays 38-46) and the primary bed 50 (corresponds to trays 19-31) are represented by the blocked out areas. The other trays are denoted by number. Tray 49 is the reboiler.

TABLE 3

	TRAY	TEMP °F	PRESSURE PSIA	LIQUID LBM/H	VAPOR LBM/H	FEED LBM/H	PRODUCT LBM/H
10	1C	131.2	114.7	1504			134.1 vap. 208.7 Liq.
15	2	251.1	114.7	2247	1846		
	3	255.4	114.9	2268	2590		
	4	257.3	115.1	2265	2611		
	5	259.0	115.3	2258	2607		
	6	260.6	115.5	2250	2601		
20	7	262.4	115.7	2240	2593		
	8	264.3	115.9	2228	2583		
	9	266.5	116.1	2214	2570		
	10	268.7	116.3	2198	2556		
	11	271.2	116.5	2182	2541		
25	12	273.8	116.7	2165	2525		
	13	276.4	116.9	2149	2508		
	14	279.1	117.1	2132	2492		
	15	281.8	117.3	2116	2475		
	16	284.4	117.5	2099	2458		
30	17	287.0	117.7	2974	2442	643.9 liq.	
	18	289.9	117.9	2936	2673		
	BED	292.0	118.1	2891	2635		
	50	293.9	118.3	2846	2590		
35		295.6	118.5	2802	2545		
		297.2	118.7	2758	2501		
		298.6	118.9	2715	2457		
		299.8	119.1	2671	2413		
		301.0	119.3	2628	2370		
40		302.1	119.5	2585	2327		
		303.1	119.7	2541	2284		
		304.0	119.9	2497	2240		
		305.0	120.1	2452	2196		
		306.0	120.3	2406	2151		
45		307.2	120.5	2358	2105		
	32	308.6	120.7	1981	2056		326.2 liq.

TABLE 3 CONTINUED

	TRAY	TEMP °F	PRESSURE PSIA	LIQUID LBM/H	VAPOR LBM/H	FEED LBM/H	PRODUCT LBM/H
5							
	BED	310.2	120.9	1968	2006		
	72	312.2	121.1	1955	1993		
		314.4	121.3	1941	1980		
10		316.7	121.5	1928	1966		
		319.1	121.7	1916	1953		
		321.4	121.9	1906	1941		
		323.5	122.1	1899	1931		
		325.4	122.3	1894	1924		
15		326.9	122.5	1890	1919		
		328.1	122.7	1888	1915		
		329.0	122.9	1887	1913		
		329.7	123.1	1886	1912		
		330.2	123.3	1886	1911		
20		330.7	123.5	1886	1911		
	47	331.0	123.7	1876	1911	108.5	vap.
	48	338.0	123.9	1925	1792		
25	49R	338.3	124.1		1841		83.4 liq.

The invention claimed is:

1. An apparatus for conducting reactive distillations comprising a first distillation column, a first primary catalyst bed for carrying out a hydrogenation of unsaturated compounds comprising diolefins, said first primary catalyst bed being positioned in said distillation column to provide a first reaction zone for diolefins in said first distillation column, a first mixed saturated/unsaturated compound feed entry below said first primary bed, a hydrogen feed below said primary bed, a bottoms line and an overhead line, said overhead line connecting to a second distillation column comprising a second primary catalyst bed for carrying out hydrogenation of unsaturated compounds comprising mono olefins from said first distillation column, said second primary catalyst bed being positioned in said distillation column to provide a first reaction zone for unsaturated compounds in said second distillation column, said overhead line from said first distillation column connecting to said second distillation column above said second primary catalyst bed and a hydrogen feed below said second primary bed.

2. The apparatus according to claim 1 wherein a first secondary catalyst bed is positioned in said first column above said first primary catalyst bed, said first secondary catalyst bed to provide a second reaction zone for diolefins remaining in said first distillation column after said first reaction zone.

3. The apparatus according to claim 1 wherein a second secondary catalyst bed is positioned in said second column below said second primary bed, said second secondary catalyst bed to provide a second reaction zone for mono olefins remaining in the second distillation column after said first reaction zone.

4. The apparatus according to claim 1 wherein a first secondary catalyst bed is positioned in said first column above said first primary catalyst bed, said first secondary catalyst bed to provide a second reaction zone for diolefins remaining in said first distillation column



after said first reaction zone and a second secondary catalyst bed is positioned in said second column below said second primary bed, said second secondary catalyst bed to provide a second reaction zone for mono olefins remaining in the second distillation column after said first reaction zone.

5. The apparatus according to claim 1 wherein a side draw is connected to withdraw a portion of the liquid in said first column into a collector, said collector being connected to said second distillation column above said second primary catalyst bed.

6. The apparatus according to claim 2 wherein a side draw is connected to withdraw a portion of the compounds in said first column below said first secondary catalyst bed into a collector, said collector being connected to said second column above said second primary catalyst bed.

7. The apparatus according to claim 1 wherein a side draw is connected to withdraw a portion of the compounds in said second column into a collector, said collector being connected to a product recovery line.

8. The apparatus according to claim 3 wherein a side draw is connected to withdraw a portion of the liquid in said second column below said second primary catalyst bed into a collector, said collector being connected to a product recovery line.

9. A process for conducting reactive distillation hydrogenations comprising

feeding hydrogen and a stream comprising hydrocarbons in a range of carbon atoms and including mono olefins and diolefins below a first primary reaction zone containing a hydrogenation catalyst under conditions of concurrent reaction and distillation to bring a key component being less than said range of carbon atoms into said first primary reaction zone containing a hydrogenation catalyst, to hydrogenate diolefins,

recovering a diolefin-depleted key component stream,
separating a stream comprising hydrocarbons of more carbon atoms than said key component,



feeding said diolefin-depleted stream above and hydrogen below a second primary reaction zone under conditions of concurrent reaction and distillation to hydrogenate mono olefins and separate hydrocarbons having fewer carbon atoms than said key component and

recovering a product comprising said key component and being mono olefin-depleted and diolefin-depleted.

10. The process according to claim 9 wherein said key component and heavier components from said second primary reaction zone enters into a second secondary reaction zone containing a hydrogenation catalyst under conditions of concurrent reaction and distillation to hydrogenate mono olefins.

11. The process according to claim 10 wherein a side draw fraction is withdrawn from said second primary reaction zone and a portion of said side draw fraction is returned to said second primary reaction zone.

12. The process according to claim 10 wherein a side draw fraction is withdrawn from said second primary reaction zone as vapor.

13. The process according to claim 9 wherein said key component and lighter hydrocarbons from said first primary reaction zone enter into a first secondary reaction zone containing a hydrogenation catalyst under conditions of concurrent reaction and distillation to hydrogenate diolefins.

14. The process according to claim 13 wherein a side draw fraction is removed from said first secondary reaction zone and a portion of said side draw fraction is returned to said first secondary reaction zone.

15. The process according to claim 9 wherein after said first primary reaction zone said key component and lighter hydrocarbons enter into a first secondary reaction zone containing a hydrogenation catalyst under conditions of concurrent reaction and distillation to hydrogenate diolefins and

after said second primary reaction zone said key component enters into a second secondary reaction zone



containing a hydrogenation catalyst under conditions of concurrent reaction and distillation to hydrogenate mono olefins.



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