July 23, 1974 G. W. VACHUDA 3,825,490

MOLECULAR SIEVE SELECTIVE ADSORPTION PROCESS

Filed Feb. 14, 1972 3 Sheets-Sheet 1

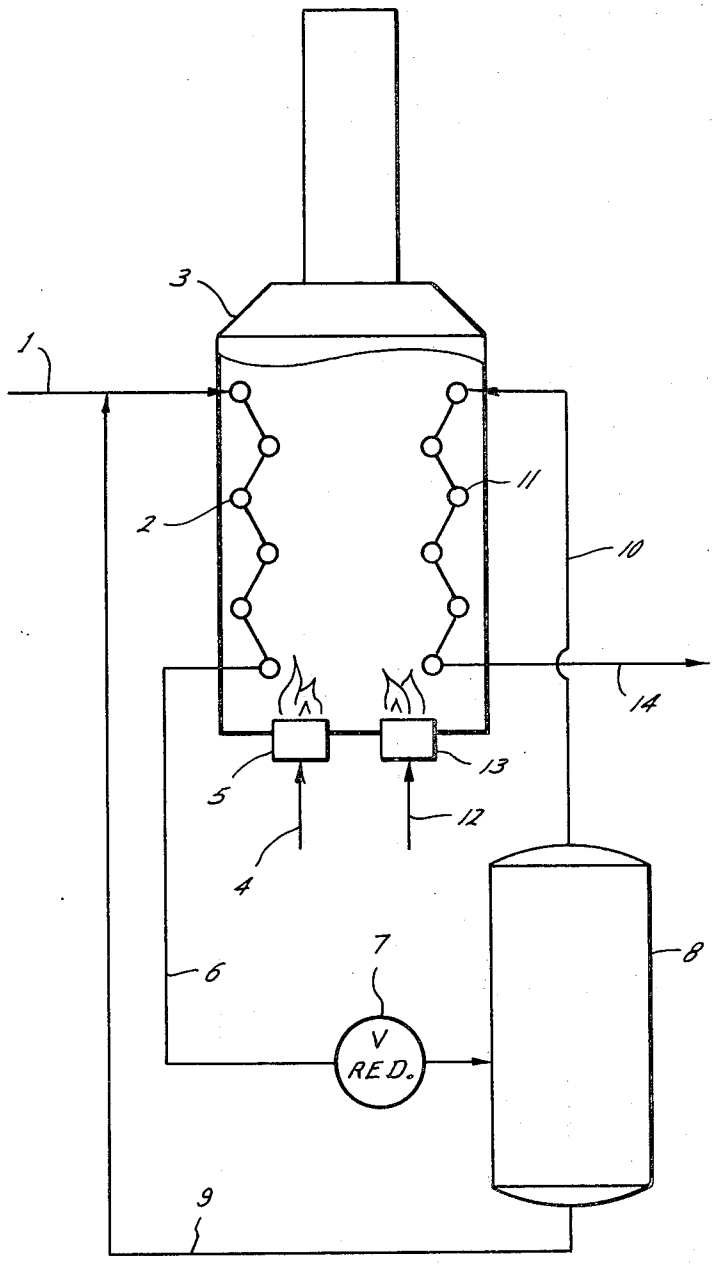


Fig. 1

MOLECULAR SIEVE SELECTIVE ADSORPTION PROCESS

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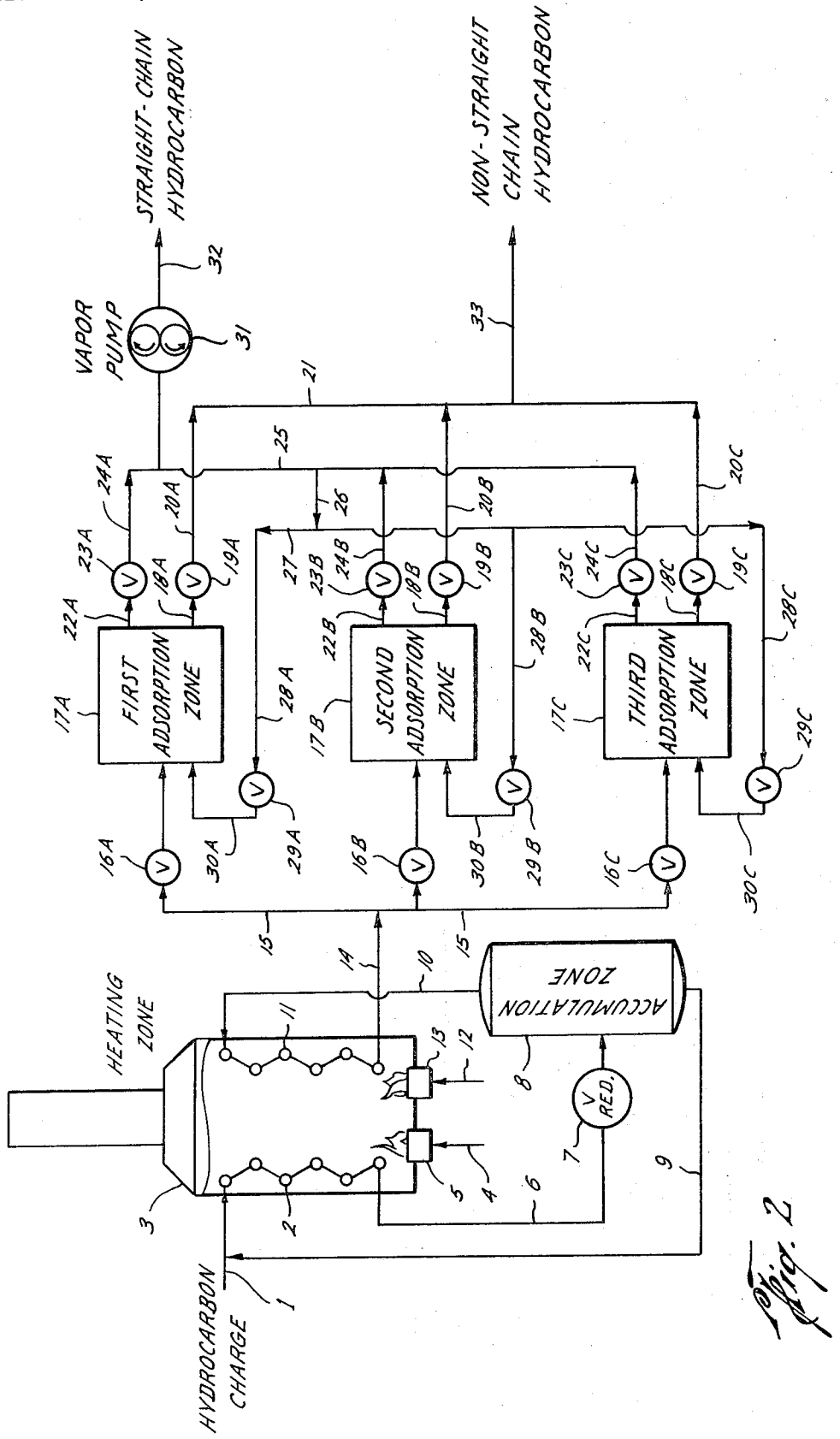


Fig. 2

MOLECULAR SIEVE SELECTIVE ADSORPTION PROCESS

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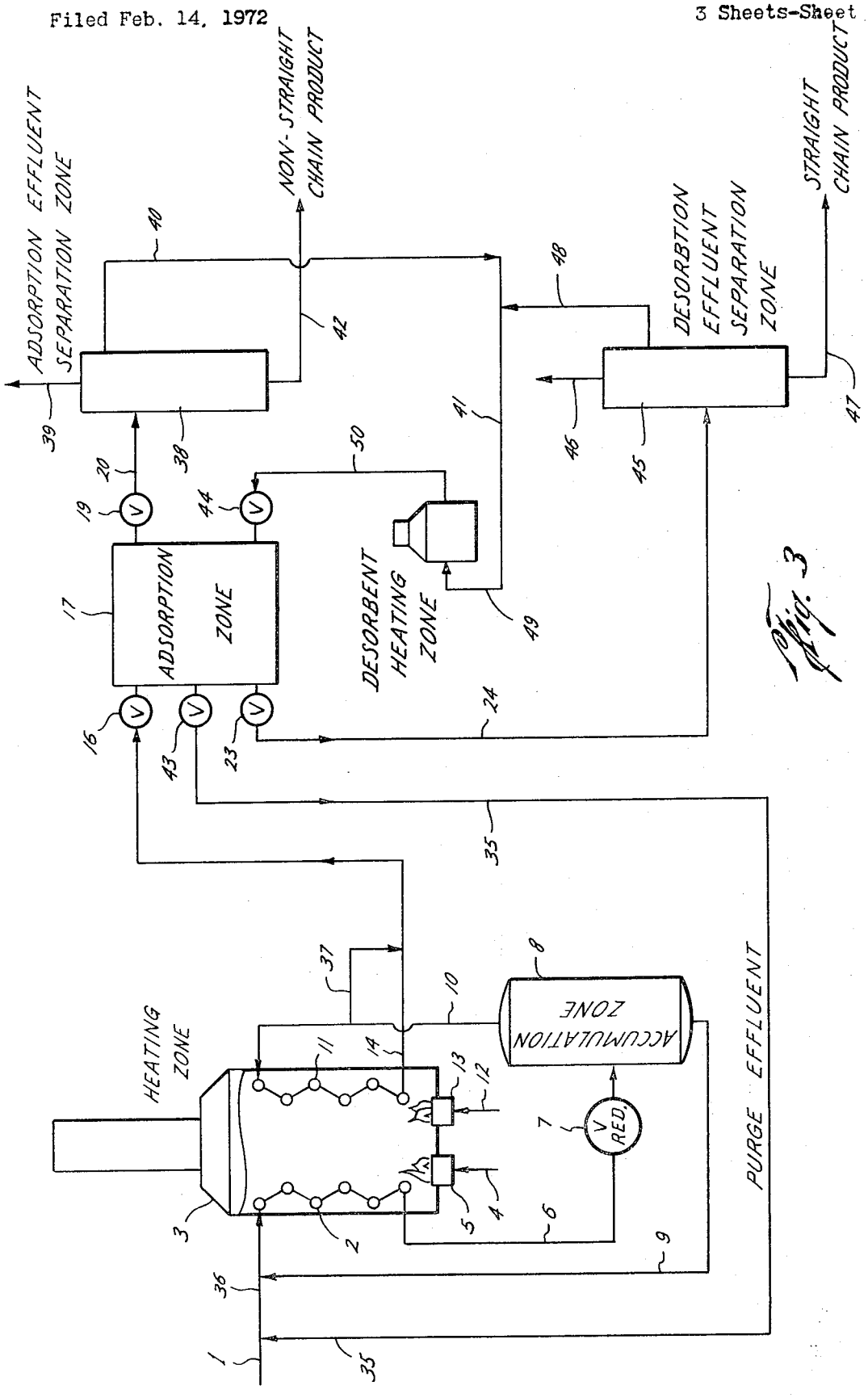


Fig. 3

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MOLECULAR SIEVE SELECTIVE ADSORPTION PROCESS

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ABSTRACT OF THE DISCLOSURE

A molecular sieve selective adsorption process for separating non-straight chain hydrocarbons from a C_5–C_9 charge mixture of straight chain and non-straight chain hydrocarbons incorporating a charge vaporization system wherein liquid charge is partially vaporized in a first heating zone at an elevated pressure, wherein partially vaporized charge is totally vaporized by adiabatic expansion in an expansion zone exterior to the heating zone, and wherein the vaporized charge is superheated in a second heating zone prior to admission into an adsorption zone.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an improved method for completely vaporizing a low molecular weight hydrocarbon stream in the C_5–C_9 carbon number range employing a heating means having a high heat flux density wherein the hydrocarbon being vaporized passess through the "dry point" outside the area of high heat flux density. More particularly, a C_5–C_9 range hydrocarbon liquid is heated, in a first heating step, at a superatmospheric pressure to vaporize about 90% of the hydrocarbon. The pressure of the hydrocarbon effluent from the first heating step is reduced to vaporize substantially all of said hydrocarbon. Additionally, hydrocarbon vapor from the pressure reduction step may be superheated, in a second heating step, employing a high heat flux density heating means.

The term "dry point," as employed in the present disclosure, means the condition of the heated hydrocarbon just as it passes from a gas-liquid mixed phase into a totally vaporized phase. The term "heat flux density," or as sometimes used herein "flux density," means the rate of heat transfer from the heat source to the hydrocarbon being heated per unit area of heat transfer surface, commonly expressed in Engineering terms as B.t.u./hr.-ft.^{2}.

An efficient means for vaporizing a light hydrocarbon in the C_5–C_9 range is to pass the hydrocarbon through a tube, or series of tubes, and provide the necessary heat by a flame external to said tubes. Commonly the tubes are arranged along the walls, or periphery, of a heating chamber comprising a refractory interior wall, and the heating flame or flames, is located at the bottom near the center of the heating chamber. In the case where the heating chamber comprises a horizontally elongated box-like structure, the heating tubes may be arranged along the wall of the chamber and the heating flames may be arranged in one or more rows parallel to the long central axis of the horizontally elongated heating chamber.

In a direct fired heater as described above, heat generated by an open flame is transferred to tubes containing a hydrocarbon by three major modes. Heat is transferred from the hot combustion gases to the tubes by convection. Heat is transferred by radiation from the visible flames to those portions of the tubes which are within the line of sight of the flames. Additionally, heat is transferred by radiation from hot refractory surfaces within the combustion chamber to the tubes. To vaporize a given amount of hydrocarbon, sufficient heat must be transferred from

that generated by the flames, through the tube walls and into the hydrocarbon to provide the sensible heat and the heat of vaporization required to vaporize such hydrocarbon. An average flux density for heat transfer is obtained by dividing the total surface area of the tube into the total amount of heat adsorbed by the hydrocarbon. However, the heat flux across different portions of the tube surface may vary greatly. For instance, for those portions of the tube surface within the line of sight of the flame which receive substantial amounts of radiant energy, the heat flux may be several times higher than heat flux for those portions of the tube surface which are not within the line of sight of the radiant flames.

Heat generated by the flames and transferred to the tubes increases the temperature of the tubes. This heat is then transferred from the tubes by conduction to the hydrocarbon flowing within such tubes. It is known that heat transfer from the tubes to the hydrocarbon proceeds at a higher rate when the hydrocarbon is at least partially in the liquid phase than when the hydrocarbon is completely in the vapor phase. Consequently, less driving force is required to transfer heat from the tubes into a hydrocarbon stream comprising liquid hydrocarbon than into a hydrocarbon stream consisting of vapors. Thus, the tube temperature where the hydrocarbon is at least partially liquid may be substantially lower than the tube temperature where the hydrocarbon is all vapor.

Different engineering design criteria must be applied to heater tubes carrying at least partially liquid hydrocarbons than applied to heater tubes carrying totally vaporized hydrocarbons in order to obtain the desired heat transfer from the flames into the hydrocarbon efficiently without overheating the tubes. In a commercial heating process the proper design of tubes for service wherein a liquid hydrocarbon charge is heated, totally vaporized, and perhaps superheated to an extent, is complicated since it is very difficult to calculate exactly where the hydrocarbon will pass from a mixed vapor-liquid phase into the total vapor phase. Changes in charge stock composition, heating value of the fuel, weather conditions, coking rate within the tubes, charge rate, etc., which are generally unpredictable with any accuracy cause the location within the tubes where hydrocarbon goes from a mixed vapor-liquid phase into a total vapor phase to change. Consequently, proper tube design to accommodate all these variables is extremely difficult and in most cases cannot be accomplished. In the event that total vaporization occurs in a section of the tube designed for mixed phase flow, the temperature of that portion of the tube may increase to an undesirably high value. When this occurs, high coking may result from contact of the hydrocarbon with the extremely hot tube surface, high rates of stress corrosion may result from sudden increases in tube temperature at such point, and tube failure may result from temperatures exceeding the design rating for the tubes.

The total vaporization of relatively low molecular weight hydrocarbons may be required in several refinery processes such as for example, thermal cracking of naphtha to produce ethylene and/or other low molecular weight hydrocarbons, vaporization of C_5–C_6 range hydrocarbons for charge to a vapor phase, catalyzed hydrocarbon isomerization process, and particularly in the vaporization of C_5–C_9 range hydrocarbons to provide a vapor feed to a molecular sieve selective adsorption process for the separation of straight chain from branched chain hydrocarbons. Molecular sieve selective adsorption processes for the separation of straight chain hydrocarbons from non-straight chain hydrocarbons in the C_5–C_9 carbon number range are well known in the art and are commercially practiced. In such processes, a hydrocarbon charge mixture comprising straight chain and non-straight chain hy-

drocarbons, in the vapor phase, at a superheated temperature, is contacted with a molecular sieve selective adsorbent. The selective adsorbent adsorbs straight chain hydrocarbons, non-straight chain hydrocarbons remain unadsorbed and pass through the selective adsorbent. Flow of hydrocarbon charge mixture may be continued to the selective adsorbent for a time period until the selective adsorbent becomes saturated with straight chain hydrocarbons. During such period a non-straight chain hydrocarbon effluent from the selective adsorbent may be separately recovered. At the end of the selected time period, or upon saturation of the selective adsorbent with straight chain hydrocarbon, flow of charge hydrocarbon to the selected adsorbent is stopped.

Such a process as above described is cyclic, comprising an adsorption cycle and a desorption cycle. Such cycles may be repeated in sequence until the selective adsorbent loses its capacity to adsorb straight chain hydrocarbon due to mechanical failure of the selective adsorbent crystalline structure or the accumulation of coke and/or other carbonaceous deposits upon the surface of the selective adsorbent. Since the separation process is cyclic, flow of hydrocarbon charge to the selective adsorbent is intermittent. Consequently, the common commercial practice is to employ a plurality of adsorption zones, each containing selective adsorbent such that at least one adsorption zone is continuously available for the adsorption cycle while other adsorption zones are upon the desorption cycle or otherwise being prepared for return to an adsorption cycle.

Non-straight chain hydrocarbons in the C_5–C_9 carbon number range, recovered as products from such molecular sieves selective adsorption process, have a substantially higher octane number than that of a mixed hydrocarbon charge to the selective adsorption process. Thus, such non-straight chain hydrocarbons are valuable as components for gasoline, since non-straight chain hydrocarbons require less chemical additives, such as tetraethyl lead, or subsequent processing to make them acceptable as motor fuel. The straight chain hydrocarbons recovered from such a selective adsorption process may be fractionated into relatively pure component fractions for use as chemicals, may be employed as hydrocarbon solvents, or may be returned to other refining processes, such as isomerization, for conversion into additional amounts of non-straight chain hydrocarbon suitable for use in motor gasoline.

Operating conditions for the adsorption of straight chain hydrocarbons from mixed hydrocarbon charge in the C_5–C_9 carbon number range include pressures in the range of from about 50 to about 200 p.s.i.g., temperatures in the range of from about 400 to about 700° F., and space velocities of from about 0.5 to about 5.0 volumes of hydrocarbon charge per hour per volume of selective adsorbent during the adsorption cycle. Operating conditions for desorption of straight chain hydrocarbons from selective adsorbent include temperatures in the range of from about 400 to about 700° F., and pressures in the range of from about 5 p.s.i.a. to about 200 p.s.i.a.

Desorption of straight chain hydrocarbons from a selective adsorbent may be accomplished at relatively high pressures in the range of from about 50 p.s.i.g. to about 200 p.s.i.g. employing a desorbent hydrocarbon vapor. A desorbent hydrocarbon vapor, preferably in the range of from 1 to 3 carbon atoms less than the adsorbed straight chain hydrocarbons, is contacted with the selective adsorbent at a temperature in the range of from about 400 to about 700° F. The partial pressure effect of the presence of the lower molecular weight desorbent hydrocarbon vapor and the concentration gradient of straight chain hydrocarbon between pores of the selective adsorbent and the vapor space surrounding such adsorbent allows a substantial portion of adsorbed straight chain hydrocarbons to pass from the selective adsorbent into the vapor phase. By maintaining a flow of desorbent hydrocarbon vapor through the selective adsorbent, the concentration of straight chain hydrocarbons in the vapor phase may be maintained at a relatively low value thereby maintaining the straight chain hydrocarbon concentration gradient. Consequently, a major portion of adsorbed straight chain hydrocarbon may be desorbed into the flowing desorbent hydrocarbon vapor stream. As straight chain hydrocarbons are desorbed from the selective adsorbent, adsorbable components of desorbent hydrocarbon vapor will enter the pores of the selective adsorbent and be adsorbed therein. Such portions of desorbent hydrocarbon which enter the selective adsorbent pores is displaced from the selective adsorbent by straight chain hydrocarbons during a subsequent adsorption step. In a subsequent adsorption step, displaced desorbent hydrocarbon is removed from the selective adsorbent in admixture with unadsorbed non-straight chain hydrocarbons.

Preferably, as stated above, desorbent hydrocarbon is selected from hydrocarbons in the range of from about 1 to about 3 carbon numbers less than the carbon number range of the hydrocarbon charged to the adsorption process. However, hydrocarbons containing less than three carbon atoms may be disadvantageous in the process. For example, when a hydrocarbon charge in a C_5–C_9 carbon number range is being charged to the adsorption process, desorbent hydrocarbon of from one to three carbon atoms less than C_5 hydrocarbons would encompass the C_2–C_4 range. It may be desirable to recover desorbent hydrocarbon for recycle as a liquid stream. Consequently, desorbent hydrocarbons having less than 3 carbon atoms may be disadvantageous because of difficulty in condensing such hydrocarbons as methane and ethane. Effluent from a desorption cycle, comprising desorbent hydrocarbon and straight chain hydrocarbons, may be conveniently separated into a desorbent hydrogen component and a straight chain hydrocarbon component by fractional distillation methods. Recovered desorbent hydrocarbon may be vaporized and heated to the desired temperature and recycled to a subsequent desorption cycle. Likewise, desorbent hydrocarbon in admixture with non-straight chain hydrocarbons contained in the effluent from an adsorption cycle, may be separated by fractional distillation means and recycled to a subsequent desorption cycle. By such recycle, desorbent hydrocarbon is conserved within the system and only small amounts of make up desorbent hydrocarbon will be required to maintain the desired circulation rate.

An alternative method for desorbing straight chain hydrocarbons from a selective adsorbent in a desorption step comprises reducing pressure upon the selective adsorbent to a value below that in the adsorption step. By reducing the pressure upon the selective adsorbent, straight chain hydrocarbons contained within pores of the selective adsorbent enter the vapor phase and may be removed from contact with the selective adsorbent. At the end of an adsorption step, the selective adsorbent containing an adsorbed straight chain hydrocarbon is at about the elevated operating temperature of the adsorption step. Upon reducing pressure upon the selective adsorbent at such an elevated temperature in the desorption step, adsorbed straight chain hydrocarbon is vaporized. For example, an adsorption step may be operated at a pressure in the range of from about 50 to about 200 p.s.i.g. at a temperature of from about 400 to 700° F. adsorbing straight chain hydrocarbon from a mixed hydrocarbon charge comprising C_5–C_9 carbon number hydrocarbons. At the end of the adsorption step, pressure upon the selective adsorbent may be reduced slightly to remove non-straight chain hydrocarbons which are present in the interstices between particles of selective adsorbent. Then, in the desorption step, pressure upon the selective adsorbent may be reduced to the range of from about 5 p.s.i.a. to about 50 p.s.i.a. such that a major portion of adsorbed straight chain hydrocarbon is vaporized and flows away from the selective adsorbent.

Selective adsorbents which may be used in such molecular sieve selective adsorption processes include those which adsorb straight chain hydrocarbons in the C_5–C_9 carbon number range and exclude non-straight chain hydrocarbons of similar carbon number range. Examples of such selective adsorbents include metal containing, crystalline, alumino-silicate zeolitic molecular sieves such as zeolite A, zeolite D, zeolite T, zeolite X, erionite, zeolite L, zeolite Y, chabozite, faujasite and mordenite as well as other adsorbents which selectively adsorb straight chain hydrocarbons to the exclusion of non-straight chain hydrocarbons. Such molecular sieve selective adsorbents have uniform pore openings in the range of about 5–14 angstrom units such that straight chain hydrocarbons may enter the molecular sieve through such pore openings and branch chain hydrocarbons are excluded therefrom. A molecular sieve particularly suitable for separating straight chain hydrocarbons from non-straight chain hydrocarbons comprises a crystalline calcium substituted sodium alumino-silicate zeolite having openings in the crystalline lattice of about 5 angstrom units.

Hydrocarbon charge stocks which may be employed in such molecular sieve selective adsorption process include petroleum fractions, shale oil fractions, etc. having a carbon number range of from about C_5–C_9 and which comprise straight chain and non-straight chain hydrocarbons For instance, such hydrocarbon fractions may be obtained from petroleum crude oil distillates, catalytically cracked light naphthas, catalytically reformed petroleum fractions, etc. Such hydrocarbon charge stock to the molecular sieve selective adsorption process may comprise paraffins, olefins, naphthines, and aromatics. Preferably, hydrocarbons containing substantial amounts of olefins and/or sulfur compounds are hydrotreated to saturate such olefins prior to charge to the selective adsorption process such that the rate of coke deposition upon the selective adsorbent is minimized.

SUMMARY OF THE INVENTION

Now according to the method of the present invention, an improvement is disclosed for totally vaporizing a C_5–C_9 carbon number range hydrocarbon wherein heat necessary for vaporization is supplied by a direct fired heating means. The improved method comprises partially vaporizing the hydrocarbon at a superatmospheric pressure in a first heating step; totally vaporizing the partially vaporized hydrocarbon effluent from the first heating step in a pressure reducing step; and superheating the totally vaporized hydrocarbon in a second heating step. Partial vaporization of the hydrocarbon in the first heating step is limited such that not more than about 90 mole percent of the hydrocarbon is vaporized in the first heating step.

An advantage for partially vaporizing the hydrocarbon in the first heating step is that a liquid phase is present in the tubes which transport the hydrocarbons through a first heating zone employed in the first heating step. The presence of a hydrocarbon liquid phase aids in the efficient transfer of heat from the tubes into the hydrocarbon. Consequently, by maintaining a hydrocarbon liquid phase, such tubes may be efficiently designed for receiving heat from a flame heat source and transmitting such heat into the hydrocarbon. An advantage for totally vaporizing the hydrocarbon in a pressure reduction step outside the first heating zone is the hydrocarbon passes through its "dry point" in an area of low heat flux so such problems as excessive coking rates, high stress corrosion rates, and excessive tube temperatures, which are associated with a hydrocarbon passing through its "dry point" in a direct fired heating zone having a high heat flux density, are substantially eliminated. The totally vaporized hydrocarbon may then be conveniently superheated to the desired degree in a second heating step having a high heat flux density employing tubes designed for the efficient transfer of heat from the flame source into the hydrocarbon vapor.

Employing such improved hydrocarbon vaporization method, an improved selective adsorption process is disclosed for separating non-straight chain hydrocarbons suitable for use in motor gasoline from a C_5–C_9 carbon number range hydrocarbon comprising straight chain and non-straight chain hydrocarbons. Such improved selective adsorption process comprises partially vaporizing a C_5–C_9 hydrocarbon mixture of straight chain and non-straight chain hydrocarbons in a first heating step, at a superatmospheric pressure; totally vaporizing, in a first pressure reduction step, the partially vaporized hydrocarbon effluent from the first heating step; superheating, in a second heating step, at a superatmospheric pressure, the hydrocarbon vapor from the first pressure reduction step; contacting, in an adsorption step, the superheated hydrocarbon vapor with a selective adsorbent at a superatmospheric pressure to adsorb straight chain hydrocarbons into said selective adsorbent and excluding non-straight chain hydrocarbons from said selective adsorbent for use as components in motor gasoline and recovering the straight chain hydrocarbons from the selective adsorbent in a desorption step.

As can be seen, the adsorption step and the desorption step of the selective adsorption process are cyclic and flow of hydrocarbon charge to the selective adsorbent is intermittent. Consequently, it is preferred to employ a plurality of adsorption zones, each containing selective adsorbent, such that adsorption zones are continuously available for the adsorption cycle while other adsorption zones are upon the desorption cycle in such a manner that flow of superheated hydrocarbon charge to the process is maintained at a substantially steady flow rate.

The advantage of the improved selective adsorption process is that liquid hydrocarbon streams in the C_5–C_9 carbon number range comprising straight chain and non-straight chain hydrocarbons may be vaporized and superheated at a superatmospheric pressure and treated with a selective adsorbent to recover non-straight chain hydrocarbons desirable for use in motor gasoline employing only a direct fired heating means before the adsorption step. The prior art means for obtaining the hydrocarbon charge in a vapor state prior to superheating said charge, such as preflash distillation columns or prefractionation columns, are eliminated.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 of the drawings is a schematic representation of a process for carrying out the improved hydrocarbon vaporization method of the present invention.

FIG. 2 of the drawings is a schematic representation of one embodiment of a selective adsorption process for the separation of non-straight chain hydrocarbons from a C_5–C_9 carbon number range hydrocarbon comprising straight chain and non-straight chain hydrocarbons wherein straight chain hydrocarbons are desorbed employing a reduced pressure in the desorption step. Such process employs the improved hydrocarbon vaporization method of the present invention.

FIG. 3 of the drawing is a schematic representation of a second embodiment of a selective adsorption process for the separation of non-straight chain hydrocarbons from a C_5–C_9 carbon number range charge comprising straight chain and non-straight chain hydrocarbons wherein desorption of straight chain hydrocarbons in the desorption step is accomplished employing a desorbent vapor. Such process employs the improved hydrocarbon vaporization method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In order to better understand the present invention, attention is now called to the drawings. FIG. 1 of the drawing is a schematic representation of a process embodying the improved vaporization method of the present

invention. For purposes of clarity, various pieces of conventional equipment such as pumps, instrumentation, valves, etc. unnecessary to properly describe the present invention have been omitted from the drawings. Such conventional equipment, its location and use, will be readily apparent to those skilled in the art. The appended drawings, and the detailed description which follows, is intended to illustrate the present invention only and is not to be interrupted as a limitation of the scope of the present invention which is set out in the appended claims.

Referring now to FIG. 1 of the drawing, a liquid hydrocarbon charge stream comprising C_5–C_6 hydrocarbons has the following analysis:

Component:	Mole percent
Isopentane	16.971
Normal pentane	26.08
Isohexane	1.29
2,3 Dimethylbutane	3.48
2 Methylpentane	18.776
3 Methylpentane	12.476
Normal hexane	13.041
Isoheptane	0.337
Methylcyclopentane	5.560
Cyclohexane	1.700
Benzene	0.275

Such liquid hydrocarbon charge at a rate of 287.01 moles per hour, a temperature of 100° F., and a pressure of 220.0 p.s.i.a. in line **1** flows through heating zone **3** within the first tubes **2** wherein the hydrocarbon charge is heated and partially vaporized. In the heating zone **3** the heat necessary to partially vaporize the hydrocarbon charge is supplied by burning natural gas from line **4** in burners **5**. Heat at a rate of 5,344.37 thousand BTU per hour (MBTU/H) is transferred from the burning gas through tubes **2** to the hydrocarbon charge.

Effluent hydrocarbon from the first tubes **2** leaving heating zone **3**, comprising about 90 mole percent vapor and about 10 mole percent liquid at a temperature of 323.34° F. and a pressure of 200.00 p.s.i.a. passes via line **6** to pressure reducing valve **7**. In pressure reducing valve **7** the effluent hydrocarbon from heating zone **3** is flashed to produce a hydrocarbon vapor stream having a temperature of 298.33° F. at a pressure of 150.00 p.s.i.a. in flash drum **8**. The vapor-liquid mixed phase hydrocarbon effluent from tubes **2** is essentially completely vaporized by expansion through pressure reducing valve **7** and no liquid phase is present in flash drum **8**. In the event that vaporation should be incomplete, any liquid phase which collects in flash drum **8** may be returned to the inlet of the first tubes **2** via line **9**. Hydrocarbon vapor at a temperature of 298.33° F., a pressure of 150 p.s.i.a., and a rate of 287.01 moles per hour is transferred from flash drum **8** via line **10** to the inlet of second tubes **11** in heating zone **3**. Hydrocarbon vapor passes through heating zone **3** within tubes **11** and heat necessary to superheat the hydrocarbon vapor is supplied by burning natural gas from line **12** in burner **13**. Heat from the burning gas is transferred through tubes **11** into the hydrocarbon vapor at a rate of 2,768.25 MBTU/H, to increase the temperature of the hydrocarbon vapor to about 500° F. Effluent hydrocarbon from heating zone **3** at a rate of 297.01 moles per hour, a pressure of about 130 p.s.i.a. and a temperature of 500° F. is recovered for further processing via line **14**.

By following this means for vaporizing and superheating a hydrocarbon liquid charge a liquid phase is maintained in first heating tubes **2**, allowing efficient heat transfer from the heat source to the hydrocarbon. By flashing and totally vaporizing, the hydrocarbon charge outside the zone of high heat flux density, problems associated with a hydrocarbon passing through its "dry point" are substantially eliminated. Causes of tube failures, such as excessive coking rates, high stress corrosion rates, and excessive tube temperatures associated with a hydrocarbon passing through its "dry point" in a direct fired heating zone are substantially eliminated. By having a totally vaporized hydrocarbon charge to the second tubes **11**, such tubes may be properly designed for the transfer of heat from the heat source to the superheated hydrocarbon vapor.

FIG. 2 of the drawings is a schematic representation of a selective adsorption process for the separation of non-straight chain hydrocarbons suitable for use in motor gasolines from a hydrocarbon mixture comprising straight chain and non-straight chain hydrocarbons. Such selective adsorption process employs the improved hydrocarbon vaporization method disclosed herein to prepare the hydrocarbon charge stock for charge to the adsorption step. In FIG. 2 hydrocarbon charge comprising about 60.87 mole percent non-straight chain hydrocarbons and about 39.13 mole percent straight chain hydrocarbons in the liquid phase at a temperature of about 100° F. at a rate of about 287.01 moles per hour in line **1** passes into tubes **2** contained within heating zone **3**. Natural gas from line **4** is burned in burner **5** to provide heat for partially vaporizing hydrocarbon charge in tubes **2**. Hydrocarbon effluent from tubes **2** comprising about 90 mole percent vapor and about 10 mole percent liquid at a pressure of about 200 p.s.i.a., and a temperature of 323.34° F. passes through line **6** to pressure reducing valve **7**. The mixed phase hydrocarbon in pressure reducing valve **7** is totally vaporized to produce 287.01 moles per hour of hydrocarbon vapor at a temperature of about 298.33° F. and a pressure of about 150 p.s.i.g. in accumulation zone **8**. The volume of accumulation zone **8** is about 25 cubic feet, sufficient to allow disengagement of any liquid which may enter with the vaporized hydrocarbon and to provide pressure surge capacity for maintaining a relatively constant pressure upon the hydrocarbon vapor charge to the following selective adsorption process. Liquid hydrocarbon condensate in accumulation zone **8** which may enter with the vaporized hydrocarbon or which may form within accumulation zone **8** passes via line **9** for admixture with additional hydrocarbon charge to the process. Hydrocarbon vapor from accumulation zone **8** passes via line **10** into tubes **11** contained within heating zone **3** for superheating. Natural gas from line **12** is burned in burner **13** to provide heat for superheating the hydrocarbon vapor contained within tubes **11**.

Superheated hydrocarbon from tubes **11** at a temperature of about 500° F., a pressure of 130 p.s.i.a. and a flow rate of 287.01 moles per hour is recovered in line **14** for charge to the selective adsorption process.

The selective adsorption process to be described is a cyclic process employing three adsorption zones. Flows to and from the adsorption cases are controlled by opening and closing appropriate valves according to which step of the cyclic process a particular adsorption zone is being employed. In the following description one cycle of the cyclic process will be described. Valves not being described as opened are to be presumed closed. Each adsorption cycle is continued for a period of 6 minutes at which time an adsorption cycle is terminated for one adsorption zone and an adsorption cycle begins for another adsorption zone.

Superheated hydrocarbon vapor from line **14** passes via line **15** through valve **16A** into a first adsorption zone **17A** wherein the superheated hydrocarbon vapor at a temperature of about 500° F. and a pressure of 130 p.s.i.a. is contacted with a selective adsorbent comprising calcium substituted sodium alumino-silicate zeolitic molecular sieve having uniform pore openings of about 5 angstrom units. Straight chain hydrocarbon components of the superheated hydrocarbon vapor enter the pores of the molecular sieve and are adsorbed therein. Non-straight chain components of the superheated hydrocarbon vapor are not adsorbed, and pass from the first adsorption zone **17A** via line **18A** through valve **19A**

and line 20A into line 21. Flow of hydrocarbon vapor to the first adsorption zone 17A is maintained for a period of 6 minutes during which time the second adsorption zone is being desorbed and the third adsorption zone is being repressured in the manner described below.

A second adsorption zone 17B, containing adsorbed straight chain hydrocarbons from a previous adsorption cycle, is upon a desorption cycle. Flow of superheated hydrocarbon charge to the second adsorption zone 17B is stopped by closing valve 16B. Within the second adsorption zone straight chain hydrocarbon is adsorbed within the selective adsorbent and a mixture of straight chain and non-straight chain hydrocarbons is present within interstices between the particles of selective adsorbent. It is desirable to recover substantially all such non-straight chain hydrocarbons for use as motor gasoline and it is also desirable to recover straight chain hydrocarbons in a relatively high degree of purity. Hydrocarbons contained within the interstices of the selective adsorbent contained within the second adsorption zone 17B pass through line 22B, valve 23B and line 24B into line 25. From line 25 the hydrocarbon effluent passes via line 26 into line 27. From line 27 such hydrocarbons pass via line 28C through valve 29C and line 30C into a third adsorption zone 17C which has previously been desorbed of straight chain hydrocarbon and is blocked in at a pressure of about 10 p.s.i.a. Flow of hydrocarbons from the second adsorption zone 17B to the third adsorption zone 17C, comprising straight chain and non-straight chain hydrocarbons, continues until the pressure within second adsorption zone 17B is decreased to about 70 p.s.i.a. The purpose of flowing hydrocarbon from the second desorption zone 17B which is being desorbed to the third adsorption zone 17C which has been desorbed and is being prepared for a subsequent adsorption step is two-fold. Non-straight chain hydrocarbons contained within the interstices of the second adsorption zone selective adsorbent are allowed to flow into the third adsorption zone and are therefore not lost from the process. Additionally, by increasing the pressure upon the third adsorption zone selective adsorbent, physical shock to the selective adsorbent is diminished when the third adsorption zone 17C is placed in an adsorption cycle and superheated hydrocarbon charge at a pressure of about 130 p.s.i.a. is suddenly allowed to enter.

When the pressure in the second adsorption zone 17B declines to about 70 p.s.i.a., valve 29C is closed and vapor pump 31 is started. Hydrocarbon effluent from the second adsorption zone 17B then flows via line 25 to vapor pump 31. Vapor pump 31 reduces the pressure within the second adsorption zone to about 10 p.s.i.a. such that a substantial portion of the straight chain hydrocarbon adsorbed upon the selective adsorbent is vaporized and is removed from the second adsorption zone 17B. Such straight chain hydrocarbon passes through vapor pump 31 into line 32 from which it is transferred to further processing, not shown. The straight chain hydrocarbon in line 32 is in a high degree of purity since substantially all non-straight chain hydrocarbons contained within the interstices of the selective adsorbent in the second adsorption zone 17B have been transferred into the third adsorption zone 17C in the previous repressuring step. When vapor pump 31 has reduced the pressure within the second adsorption zone 17B to 10 p.s.i.a., a substantial portion of adsorbed straight chain hydrocarbons have been desorbed and recovered. The desorption step is stopped by closing valve 23B and stopping vapor pump 31. The second adsorption zone is then ready for a repressuring step as described above for the third adsorption zone 17C. The non-straight chain hydrocarbons recovered from an adsorption cycle in line 21 pass into line 33 from which they are transferred to storage, not shown, for use in motor gasoline. Such non-straight chain hydrocarbons are substantially free of straight chain hydrocarbon components.

FIG. 3 of the drawing is a schematic representation of a selective adsorption process for the separation of non-straight chain hydrocarbons suitable for use in motor gasoline from a hydrocarbon charge mixture comprising straight chain and non-straight chain hydrocarbons. Such selective adsorption process employs the improved hydrocarbon vaporization method disclosed herein to prepare the hydrocarbon charge mixture for charge to an adsorption step. This embodiment of the selective adsorption process employs a desorbent vapor in a desorption of straight chain hydrocarbons from the selective adsorbent. The selective adsorption process disclosed here below is cyclic. Thus, for clarity, one complete cycle of the selective adsorption process will be described with reference to only one adsorption zone. However, it is to be understood that a plurality of adsorption zones may be employed, preferably with each upon a time cycle such that a relatively constant flow rate of hydrocarbon charge mixture is maintained to the process.

In FIG. 3, hydrocarbon charge from line 1 comprising about 60.87 mole percent non-straight chain hydrocarbons and about 39.13 mole percent straight chain hydrocarbons in the liquid phase at a temperature of about 100° F. is mixed with purge effluent, as hereinafter described, from line 35 in line 36. From line 36 the hydrocarbon mixture passes into heating tubes 2 contained within heating zone 3. Natural gas from line 4 is burned in burner 5 to provide heat for partially vaporizing the hydrocarbon mixture in heating tubes 2. Effluent from heating tubes 2, comprising about 90 mole percent vapor and about 10 mole percent liquid, at a pressure of about 200 p.s.i.a. and a temperature of 323° F. passes through line 6 to pressure reducing valve 7. The mixed phase hydrocarbon is passing through pressure reducing valve 7 is totally vaporized at a temperature of 298° F. and a pressure of about 150 p.s.i.g. in accumulation zone 8. Accumulation zone 8 has a cross section area and volume sufficient to allow disengagement of any liquid from the vaporized hydrocarbon and to provide surge capacity for maintaining a relatively constant pressure upon the hydrocarbon vapor charge to the adsorption zone. Should any liquid hydrocarbon condense or otherwise accumulate in accumulation zone 8, such liquid hydrocarbon may be transferred via line 9 to line 36 for revaporization in heating zone 3 as hereinabove described. Hydrocarbon vapor from accumulation zone 8 passes via line 10 into heating tubes 11 contained within heating zone 3, wherein the hydrocarbon vapor is superheated. Natural gas from line 12 is burned in burner 13 to provide heat for superheating the hydrocarbon vapor contained within heating tubes 11.

Superheated hydrocarbon vapor from heating tubes 11 at a temperature of about 500° F. and a pressure of about 130 p.s.i.a. is recovered in line 14 for charge to adsorption zone 17. If desired, a minor portion of hydrocarbon vapor from line 10 may be transferred via line 37 for admixture with superheated hydrocarbon vapor in line 14 to control the temperature of the superheated hydrocarbon vapor at a selected value.

In an adsorption step, superheated hydrocarbon vapor from line 14 passes through valve 16 into adsorption zone 17. Adsorption zone 17 contains a selective adsorbent comprising calcium substituted sodium alumino-silicate zeolitic molecular sieve having uniform pore openings of about 5 angstrom units. At a temperature of about 500° F. and a pressure of about 130 p.s.i.a. the selective adsorbent adsorbs straight chain hydrocarbon components of the superheated hydrocarbon vapor. From a previous desorption step, as hereinafter described, desorbent hydrocarbon, comprising C_3–C_4 straight chain hydrocarbons, is adsorbed within the pores of the selective adsorbent at the beginning of the adsorption step. In the course of the adsorption step, desorbent hydrocarbon is displaced from the selective adsorbent by C_5–C_9 straight chain hydrocarbon components of the hydrocarbon charge. From ad-

sorption zone **17** an adsorption effluent, comprising C_5–C_9 non-straight chain hydrocarbons and C_3–C_4 straight chain desorbent hydrocarbon, passes through valve **19** and line **20** into adsorption effluent separation zone **38**. In adsorption effluent separation zone **38** the effluent is separated into a C_5–C_9 range non-straight chain hydrocarbon component, a C_3–C_4 range desorbent component and a C_1–C_2 range noncondensable vapor component. The noncondensable vapor component may result from cracking of a small amount of the hydrocarbon charge at an elevated temperature in the presence of the selective adsorbent. From adsorption effluent separation zone **38**, noncondensable vapor is vented via line **39**. Desorbent hydrocarbon component is recovered via line **40** and passed into line **41** for recycle to the selective adsorption process, as hereinafter described. The C_5–C_9 range non-straight chain hydrocarbon component of the adsorption effluent is recovered from separation zone **38** via line **42**. Such non-straight chain hydrocarbon component is in a substantial degree of purity and is suitable for use in gasoline motor fuel.

The adsorption step is continued for a period of about 6 minutes. At the end of which time period the adsorption step is discontinued and a purge step is begun. In the purge step, unadsorbed hydrocarbon vapors contained within the interstices of the selective adsorbent, comprising a mixture of straight chain, non-straight chain, and desorbent hydrocarbons is purged from adsorption zone **17** prior to desorbing the straight chain hydrocarbons. At the beginning of the purge step, valves **16** and **19** are closed and purge effluent valve **43** is opened. Hydrocarbon vapor in adsorption zone **17** at a pressure of about 130 p.s.i.a. flows through valve **43** and line **35**, reducing pressure within adsorption zone **17** to about 20 p.s.i.a. Upon reduction of pressure within adsorption zone **17** to about 20 p.s.i.a., valve **44** is opened and desorbent vapor at a temperature of about 500° F. enters adsorption zone **17** for a time period of from about 1 to about 20 seconds to displace any remaining unadsorbed non-straight chain hydrocarbons. Flow of purge effluent continues through valve **43** and line **35**. From line **35** purge effluent is mixed with fresh hydrocarbon charge from line **1** in line **36**, as has been hereinabove described. At the end of the selected purge time period, valve **43** is closed and flow of desorbent hydrocarbon vapor at a temperature of about 500° F. is continued from valve **44** to increase the pressure within adsorption zone **17** to about 150 p.s.i.a.

Upon repressuring adsorption zone **17** to about 150 p.s.i.a., valve **23** is opened and a desorption step is begun. In the desorption step, the flow of desorbent vapor from valve **44** is continued and straight chain hydrocarbons are desorbed from the selective adsorbent. A portion of the desorbent hydrocarbon, comprising C_3–C_4 straight chain hydrocarbons, upon displacing the C_5–C_9 straight chain hydrocarbons is adsorbed within the selective adsorbent. Such adsorbed C_3–C_4 straight chain hydrocarbons are displaced from the selective adsorbent by C_5–C_9 straight chain hydrocarbons in a subsequent adsorption step as has hereinabove been described. A desorption effluent comprising C_5–C_9 straight chain hydrocarbons and C_3–C_4 desorbent hydrocarbons flows from adsorption zone **17** through valve **23** via line **24** to desorption effluent separation zone **45**.

In desorption effluent separation zone **45**, desorption effluent is separated into a C_5–C_9 straight chain component, a C_3–C_4 desorbent hydrocarbon component, and a C_1–C_2 noncondensable vapor component. The noncondensable vapor component is vented from separation zone **45** via line **46**. The C_5–C_9 straight chain hydrocarbon component is recovered as product from separation zone **45** via line **47** for use in other chemical processes. Desorbent hydrocarbon component is recovered from separation zone **45** via line **48** and passes into line **41**.

In line **41**, desorbent hydrocarbon component from separation zone **45** is combined with desorbent hydrocarbon component from separation zone **38**, as hereinabove described. The combined desorbent hydrocarbons are recycled to the selective adsorption process. From line **41** desorbent hydrocarbon recycle, comprising C_3–C_4 hydrocarbons, passes into desorbent heating zone **49** wherein desorbent recycle is vaporized at a temperature of about 500° F. and a pressure of about 150 p.s.i.a. From desorbent heating zone **49**, the superheated desorbent vapor passes via line **50** to valve **44**. From valve **44** desorbent vapor is admitted to adsorption zone **17** during a purge step and a desorption step, as hereinabove described.

The desorption step is continued for a time period of about 5½ minutes, such that the combined elapsed time for the purge step and the desorption step is equal to the adsorption step time period of 6 minutes. In the desorption step, substantially all the C_5–C_9 straight chain hydrocarbons are desorbed from the selective adsorbent. Upon completion of the desorption step, valves **44** and **23** are closed and valves **16** and **19** are opened thus beginning an adsorption step in a new cycle of the selective adsorption process.

By following the method of this invention, a hydrocarbon in the C_5–C_9 carbon number range may be vaporized in a direct fired heating means and superheated therein without such hydrocarbon passing through its "dry point" within the high heat flux density area of the heating means. Consequently, problems which occur at the "dry point," such as increased coking rate, high stress corrosion rate, and high tube temperatures are avoided.

A hydrocarbon mixture in the C_5–C_9 carbon number range comprising straight chain and non-straight chain hydrocarbons may be treated in a selective adsorption process employing the improved hydrocarbon vaporization method disclosed herein to yield non-straight chain hydrocarbons which are desirable components of motor gasoline. Refinery process streams such as straight run naphthas, fluid catalytically cracked naphthas, coker naphthas and effluent from catalytic reforming units, which comprise hydrocarbons of the desired carbon number range may be charged directly to the selective adsorption process without the necessity of preflash or prefractionation columns to vaporize said hydrocarbons prior to superheating them as charge stocks to the selective adsorbent.

As will be apparent to those skilled in the art upon reading the foregoing disclosure, many modifications, substitutions, and changes are possible in the practice of this invention without departing from the spirit and scope thereof. Therefore, no limitations to the present invention are intended except those contained within the spirit and scope of the appended claims.

I claim:

1. In a molecular sieve selective adsorption process for separating non-straight chain hydrocarbons from a hydrocarbon charge comprising C_5–C_9 carbon number range straight chain and non-straight chain hydrocarbons, which process comprises an adsorption step and a desorption step, wherein superheated hydrocarbon charge vapor at a temperature in the range of from about 400° F. to about 700° F. and at a superatmospheric pressure in the range of from about 50 p.s.i.g. to about 200 p.s.i.g. is contacted with a molecular sieve selective adsorbent in the adsorption step to adsorb straight chain hydrocarbons, wherein unadsorbed non-straight chain hydrocarbons are removed from the selective adsorbent, and wherein adsorbed straight chain hydrocarbons are recovered from the selective adsorbent in a desorption step; the improvement which comprises:

(a) vaporizing, in a first direct fired heating zone, from about 80 to about 95 volume percent of the C_5–C_9 hydrocarbon charge at a superatmospheric pressure;

(b) totally vaporizing partially vaporized hydrocarbon charge from said first direct fired heating zone in an adiabatic expansion zone;

(c) accumulating, in an accumulation zone, totally vaporized hydrocarbon from said adiabatic expansion zone;

(d) adjusting pressure drop across said adiabatic expansion zone for maintaining hydrocarbon charge totally vaporized at a desired steady pressure in the accumulation zone;

(e) superheating, in a second direct fired heating zone, said totally vaporized hydrocarbon charge from the accumulation zone; and

(f) supplying superheated hydrocarbon charge vapor from said second direct fired heating zone at a relatively constant superatmospheric pressure to an adsorption step in the molecular seive selective adsorption process.

2. The process according to Claim 1 wherein a plurality of adsorption zones containing selective adsorbent are employed upon timed cycles of adsorption steps and desorption steps such that superheated hydrocarbon vapor flows continuously from the second heating zone to at least one adsorption zone.

3. The method of Claim 2 wherein an absorption step is operated at a temperature in the range of from about 400° F. to about 700° F. and a pressure in the range of from about 50 p.s.i.g. to about 200 p.s.i.g., and wherein C_5–C_9 range straight chain hydrocarbons are desorbed from selective adsorbent, in a desorption step, at a temperature in the range of from about 400° F. to about 700° F. and a pressure in the range of from about 5 p.s.i.a. to about 50 p.s.i.a.

4. The method of Claim 2 wherein an adsorption step is operated at a temperature in the range of from about 400° F. to about 700° F. and a pressure in the range of from about 50 p.s.i.g. to about 200 p.s.i.g., wherein unadsorbed non-straight chain hydrocarbons are removed from interstices of selective adsorbent in a purge step, at a pressure in the range of from about 20 p.s.i.a. to about 50 p.s.i.a. by purging the selective adsorbent with desorbent hydrocarbon vapor comprising hydrocarbons in the range of from one to three carbon numbers less than the hydrocarbon charge, wherein adsorbed C_5–C_9 straight chain hydrocarbons are desorbed, in a desorption step, at a pressure in the range of from about 50 p.s.i.g. to about 200 p.s.i.g. in the presence of a flowing stream of desorbent hydrocarbon vapor at a temperature in the range of from about 400° F. to about 700° F.

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