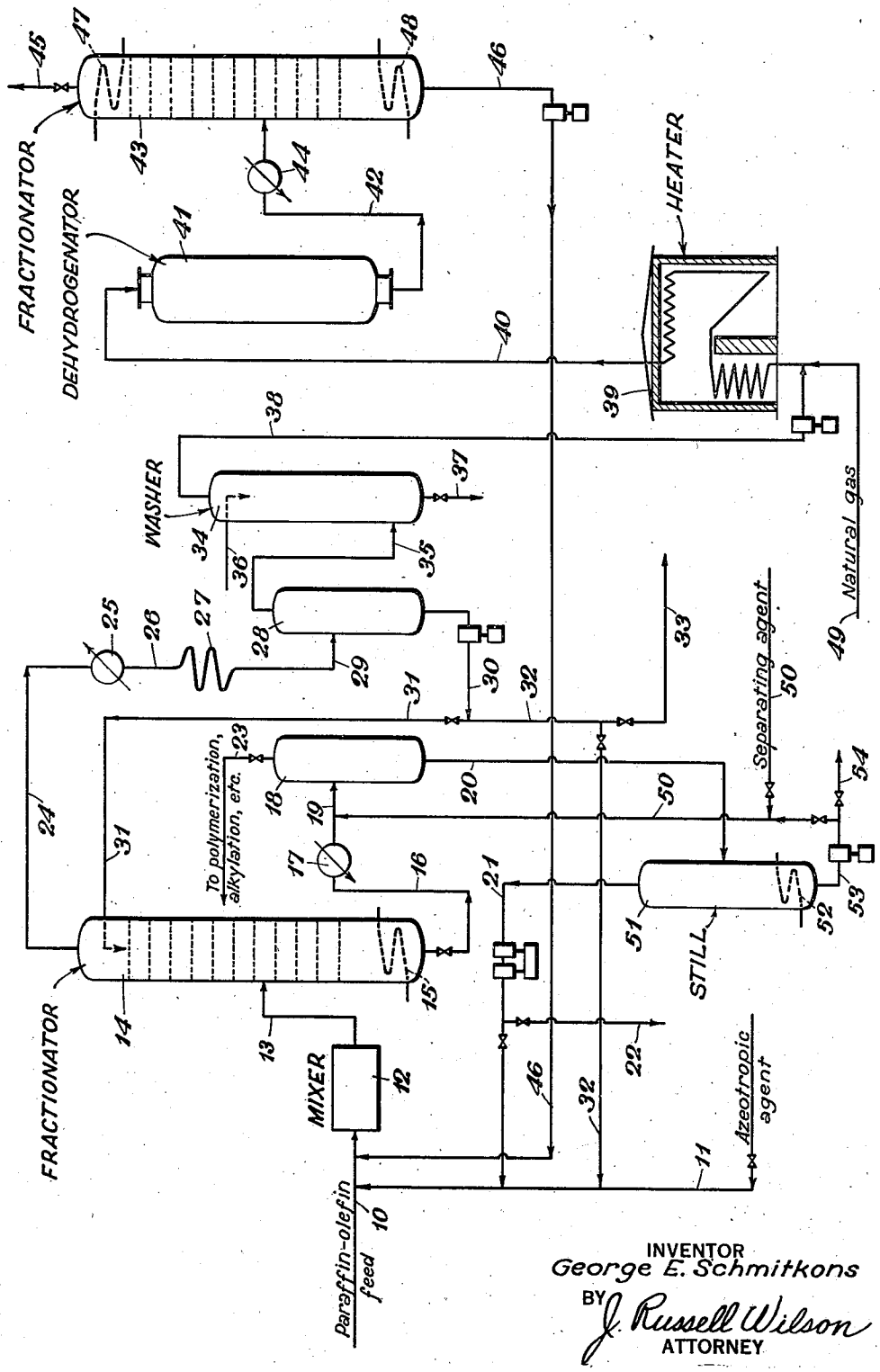
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OLEFIN PRODUCTION

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OLEFIN PRODUCTION

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This invention relates to an improved process for the production of olefins from a paraffin-olefin mixture and particularly to the production of olefins from a mixture composed almost entirely of saturated and unsaturated hydrocarbons having the same number of carbon atoms.

In recent years olefins have become more and more valuable because of the commercial success and expansion of synthetic processes for converting them into various chemical products, hydrocarbon motor fuels and lubricants, etc. This is particularly true of the so-called normally gaseous olefins which include ethylene, propylene and the butylenes. Such olefins are particularly adapted to polymerization reactions wherein products ranging from gasoline to resins are produced, to the alkylation of paraffinic or aromatic hydrocarbons or their derivatives, to the manufacture of alcohols and glycols, and to various other similar processes.

In order to control the type of product obtained, it has been found advisable in most cases to use a feed stock containing a predominating amount of only one olefin, i. e., the olefins present should be chiefly ethylene, or propylene, or butylenes, but not mixtures of any two, or all three, of the olefins.

One source of olefins for such processes as have been mentioned is the gases obtained in the cracking of oils. Other sources include the gases from the production of hydrocarbons by the Fischer-Tropsch process, the off-gases from selective polymerization, etc. Such gases, however, contain in varying amounts the corresponding saturated hydrocarbons such as ethane, propane and the butanes together with methane and hydrogen, but they may be and often are separated into fractions, each fraction of which, excluding hydrogen and methane, will predominate in two, three, or four carbon atom constituents. It has been found that the paraffinic constituents of such gases do not react with the same ease as the olefins and, in some cases, even deter or prevent the olefins from reacting to the best advantage.

It is an object of my invention to convert gas mixtures predominating in hydrocarbons having the same number of carbon atoms containing both paraffins and olefins, to a predominantly olefinic product having the same carbon atom content. It is another object of my invention to provide an integrated process for the conversion of paraffin hydrocarbons to olefin hydrocarbons and the separation of the latter in relatively pure form. A further object of my invention is to provide a novel and economical method of preparing an olefinic feed stock for hydrocarbon or other syntheses. Other and more detailed objects of my invention will become apparent as the description thereof proceeds.

In brief my invention contemplates the separation of paraffins from olefins having the same number of carbon atoms by means of azeotropic distillation, the conversion of the paraffins to olefins by dehydrogenation, preferably catalytic dehydrogenation, and the separation of the converted from the unconverted paraffins by the original azeotropic distillation means.

Paraffins can be separated from the corresponding olefins by adding to the mixed paraffins-olefins a third substance which forms an azeotrope. The azeotropes of the paraffins and olefins show a greater spread in boiling point than the original paraffins and olefins, and the azeotropes can therefore be separated by distillation.

For example, the various butanes and butenes, all of which may be found in a "butane" cut from cracking still gas, have the following boiling points:

	°C.		°C.
Isobutane	−12.4	N-butane	−0.6
Isobutylene	−6.7	2-butene (trans)	1.3
1-butene	−6.7	2-butene (cis)	3.7

It will be noted that the boiling points of isobutylene and 1-butene lie between those of isobutane and normal butane, so that separation of the paraffins from the olefins by ordinary distillation into two fractions, is impossible. However, when sulfur dioxide is added to form the azeotrope, the following approximate boiling points for the azeotropes have been found:

	°C.
Azeotrope of isobutane	−24
Azeotrope of N-butane	−18
Azeotrope of 1-butane	−16
Azeotrope of isobutylene	−14
Azeotrope of 2-butene (trans)	−14
Azeotrope of 2-butene (cis)	−13

There is a spread of 2° C. between the highest boiling paraffin azeotrope and the lowest boiling olefin azeotrope, and hence separation by fractional distillation is possible.

Substances other than sulfur dioxide may be used to form azeotropic mixtures. For example, Deansley, in his United States Patent No. 1,866,800 describes the separation of butanes and butenes by azeotropic distillation, using liquid ammonia or methylamine, to give a yield of 96% butene from the butenes present. Other substances may also be used, and since the particular substance to be added to the paraffin-olefin mixture to form azeotropes is no part of my invention, they will hereinafter be referred to as "azeotropic agents."

The operation of my process will be understood from the following description and the accompanying drawing which represents a simplified flow diagram of one embodiment of my process.

Various pumps, valves, etc. have been omitted for the sake of clarity, since the necessity for their use will be readily understood by one skilled in the art who wishes to practice my invention.

A mixed paraffin-olefin feed containing predominantly hydrocarbons of the same number of carbon atoms from any suitable source, as for example plant "butane" from the stabilization of gasoline, enters through line 10 and is joined by an azeotropic agent from line 11. The two substances are thoroughly mixed in mixer 12 which may be any suitable device for intimately contacting the two streams.

The combined streams enter fractionating tower 14 by line 13 where they are heated by heater 15 which may be a closed steam coil or any other suitable means. The paraffins plus the azeotropic agent are distilled overhead and the olefins plus the remaining azeotropic agent remain as a bottom fraction. This latter mixture is withdrawn through valved line 16, cooled if desired in cooler 17, and transferred to separator 18 by line 19. Since phase separation of the azeotropic agent from the olefins cannot be accomplished by cooling alone, as can be done with paraffin azeotropes, I prefer to use a separating agent. This separating agent may be water if the azeotropic agent is relatively soluble therein, or it may be an aqueous solution of a compound with which the azeotropic agent forms a water soluble complex, easily decomposable to yield the azeotropic agent unchanged. Such compounds include the water soluble organic amines, such as pyridine and triethanol amine, alkali thiocyanates, such as sodium thiocyanate and potassium thiocyanate, and the alkali iodides, such as potassium iodide and sodium iodide, if the azeotropic agent is sulfur dioxide.

To obtain the separation of the azeotropic agent (e. g., SO_2) and the olefins, the separating agent, in an aqueous medium, is added to separator 18 through line 50 which joins line 19. The sulfur dioxide forms a loose complex with the separating agent, it is believed, and the complex is withdrawn from separator 18 through line 20 and directed to still 51, wherein it is heated by heating means 52 sufficiently to decompose the complex and drive off the sulfur dioxide as a gas. The temperature necessary to decompose the complex will vary with the separating agent chosen, but in all cases it should be less than the boiling point of water to avoid contaminating the azeotropic agent with any great amount of water vapor. The azeotropic agent passes overhead through line 21, is dried if necessary (by means not shown) and returned to the azeotropic distillation step through line 11. The separating agent is withdrawn from still 51 and returned to separator 18 for reuse through line 53, which joins line 50, or may be withdrawn from the system through line 54.

The olefins are withdrawn through line 23 and sent to a washing step (not shown) where any remaining traces of the azeotropic agent may be removed and the olefin transferred to a polymerization unit, an alkylation unit, an alcohol manufacturing process, or any other process in which the use of highly concentrated olefins is particularly advantageous.

The paraffins plus the azeotropic agent pass overhead from fractionator 14 through line 24 and condenser 25 where they are reduced to a liquid state. From condenser 25 they pass through line 26 and are further cooled in cooler 27, which reduces the temperature to such a degree that a ready separation between the paraffin and the azeotropic agent may be accomplished. The cold liquor is sent to separator 28 through line 29. In separator 28 a very substantial separation of the paraffin from the azeotropic agent takes place and the azeotropic agent is withdrawn through line 30 and a part thereof is returned to the top of fractionator 14 through line 31 to act as reflux in the distillation. The remainder of the azeotropic agent may be withdrawn through line 32 and returned to the treating system through line 11, or may be withdrawn from the system entirely through line 33.

The paraffins from separator 28 are fed to washer 34 by line 35 wherein the traces of azeotropic agent remaining are removed. The washing medium may be any suitable substance, for example, water, dilute caustic, dilute acid, etc., which will remove the azeotropic agent from the paraffins and the selection of this medium will be governed entirely by the nature of the azeotropic agent. The washing medium enters through line 36 and is discharged through line 37.

The paraffins from washer 34 are led through line 38 to heater 39 where they are raised to a temperature suitable for dehydrogenation. The heated gases pass from heater 39 through line 40 to dehydrogenator 41 which is filled with any suitable catalytic material as will be discussed later. The dehydrogenated product is withdrawn through line 42 and sent to fractionator 43 after having been cooled by cooler 44.

In fractionator 43, having reflux means 47 and heating means 48, the light gases, for example, hydrogen and methane, and any ethane and propane with their accompanying olefins, are separated and discharged from the system through line 45, while the dehydrogenated butanes and any undehydrogenated butanes are withdrawn by line 46 and returned to the azeotropic distillation system through line 10 where they join the fresh feed.

It may be desirable to use my process for the conversion of natural gas to olefins. Since natural gas contains a preponderance of paraffins and only small amounts of olefins, it is necessary to subject it to dehydrogenation before azeotropic distillation. In this event, the hydrocarbon mixture of paraffins and olefins preferably having four carbon atoms to the molecule, may be injected through line 49 just prior to heater 39, and the dehydrogenated products cycled to the azeotropic distillation step, where the olefins formed are separated from the unconverted paraffins, and the paraffins recycled to the dehydrogenation step. Other normally gaseous hydrocarbons having four carbon atoms and predominantly paraffinic, such as off-gases from alkylation, etc., would be injected at this point.

The typical operation will serve to illustrate my process. A plant "butane" cut obtained from the gases from the cracking of oil consists of both normal and isobutane, as well as isobutylene and 1- and 2-butenes. This may be mixed with sulfur dioxide in the proper proportions to obtain the best separation which generally requires an excess of sulfur dioxide over that required to form the azeotropes and the mixture subjected to distillation at approximately 0° F. to 125° F. and at an absolute pressure of from 15 to 150 pounds per square inch. The butene azeotropes having a higher boiling point than the azeotropes of butane and isobutane will collect in the bottom of fractionator 14. After cooling and removing the sulfur dioxide, it will be found that approxi-

mately 95% or more of the butenes contained in the original plant "butane" have been recovered in this manner.

The butenes from the azeotropic distillation (which term is intended to include isobutylene) will be found to be a most excellent feed stock for polymerization to gasoline using as a catalyst such well known agents as phosphoric acid on kieselguhr or boron fluoride. It is also an excellent feed stock for polymerization at low temperatures with such gaseous metallic halides as boron fluoride to high molecular weight resins. If desirable the isobutylene present may be selectively polymerized to yield high octane gasoline and the normal butenes remaining may then be isomerized over such catalysts as phosphorus pentoxide or phosphoric acid on kieselghur at other temperatures, pressures and time of contact. Such isomerized olefins may then be returned to the selective polymerization step for polymerization of high octane gasolines. Other uses for olefins will readily occur to those skilled in the art, and my invention is not directed to the specific utilization of this valuable source material.

The butanes plus sulfur dioxide in the form of azeotropes are thoroughly cooled to permit the separation of the butanes and the sulfur dioxide, and the sulfur dioxide returned part to the fractionator to act as reflux and aid in distillation which separates the butane azeotropes from the butene azeotropes, and part returned to be mixed with the incoming plant butane feed. In this manner the amount of sulfur dioxide required is reduced to a minimum and by using a part as reflux a better fractionation is obtained.

The separated butanes are washed to remove residual sulfur dioxide and are then heated to from about 850° to about 1000° F. in heater 39. The heated gases are then passed to a catalyst chamber 41 filled with a dehydrogenating catalyst. Any suitable catalyst may be employed: chromic oxide gels, mixed alumina-chromium oxides, metal chromites, mixed alumina-metal chromites, metals or metal oxides supported on metal chromites, etc. In this manner approximately 50% of the butanes may be converted to butenes and isobutylene. In addition a certain amount of methane and higher will be formed as well as the hydrogen from the dehydrogenation. These gases are separated from the butane-butene mixture in fractionator 43 and discharged from the system. The paraffin-olefin mixture resulting from the dehydrogenation and fractionation is returned to the azeotropic distillation system where it joins fresh feed and the olefins formed are removed in the manner described previously.

It will be seen that by my process I obtain a maximum yield of olefins suitable for the synthesis of higher hydrocarbons by a completely integrated and coordinated system, no part of which can serve to accomplish my improved result independently. Azeotropic distillation alone requires the discard of gases which may be converted to a valuable and useful form. The dehydrogenation by itself is not sufficiently complete to convert all of the butanes to their olefinic form. By my process all of the paraffins are eventually converted to olefins with practically no loss, thereby providing a valuable source material for hydrocarbon synthesis.

The above description is by way of example and not by way of limitation and my invention should not be limited thereby but only insofar as is set forth in the appended claims.

I claim:

1. In a process for the production of normally gaseous olefins from a hydrocarbon mixture comprising normally gaseous paraffinic and olefinic hydrocarbons having the same number of carbon atoms, the steps comprising adding to said hydrocarbon mixture sulfur dioxide to form an azeotropic mixture therewith, distilling said azeotropic mixture into a fraction containing predominantly paraffinic azeotropes and a fraction containing predominantly olefinic azeotropes, cooling said paraffinic azeotrope until a separation of paraffinic hydrocarbons and sulfur dioxide is obtained, separating said paraffinic hydrocarbons and said sulfur dioxide, cooling said olefinic azeotrope, adding to said cooled olefinic azeotrope a separating agent comprising an aqueous solution of a compound selected from the group consisting of water-soluble organic amines, alkali thiocyanates and alkali iodides, recovering olefinic hydrocarbons present in said olefinic azeotrope from sulfur dioxide and said separating agents, subjecting said separated paraffinic hydrocarbons to dehydrogenation to convert a substantial amount but substantially less than all of said paraffinic hydrocarbons to olefinic hydrocarbons having the same number of carbon atoms and to produce a small amount of hydrocarbons having a lesser number of carbon atoms than the hydrocarbons of the first-mentioned hydrocarbon mixture, separating said hydrocarbons having a lesser number of carbon atoms formed in said dehydrogenation from said olefinic hydrocarbons having the same number of carbon atoms as said separated paraffinic hydrocarbons, returning said olefinic hydrocarbons and unconverted paraffinic hydrocarbons to be mixed with said sulfur dioxide and separating said unconverted paraffinic hydrocarbons from said olefinic hydrocarbons by azeotropic distillation.

2. A process for the production of butylenes from a mixture of butanes and butylenes, comprising adding to said mixture sulfur dioxide to form an azeotropic mixture, distilling said azeotropic mixture into a fraction containing predominantly butane azeotropes and a fraction containing predominantly butylene azeotropes, cooling said butane azeotropes until a separation of butanes and sulfur dioxide is obtained, separating said butanes and said sulfur dioxide, cooling said butylene azeotropes, adding to said cooled butylene azeotropes a separating agent comprising an aqueous solution of a compound selected from the group consisting of water-soluble organic amines, alkali thiocyanates and alkali iodides, recovering butylenes present in said butylene azeotropes from sulfur dioxide and said separating agent, catalytically dehydrogenating said separated butanes to produce butylenes and lighter hydrocarbons, separating said lighter hydrocarbons from said last-mentioned butylenes and unconverted butanes, and recycling said last-mentioned butylenes and said unconverted butanes to said azeotropic distillation step.

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