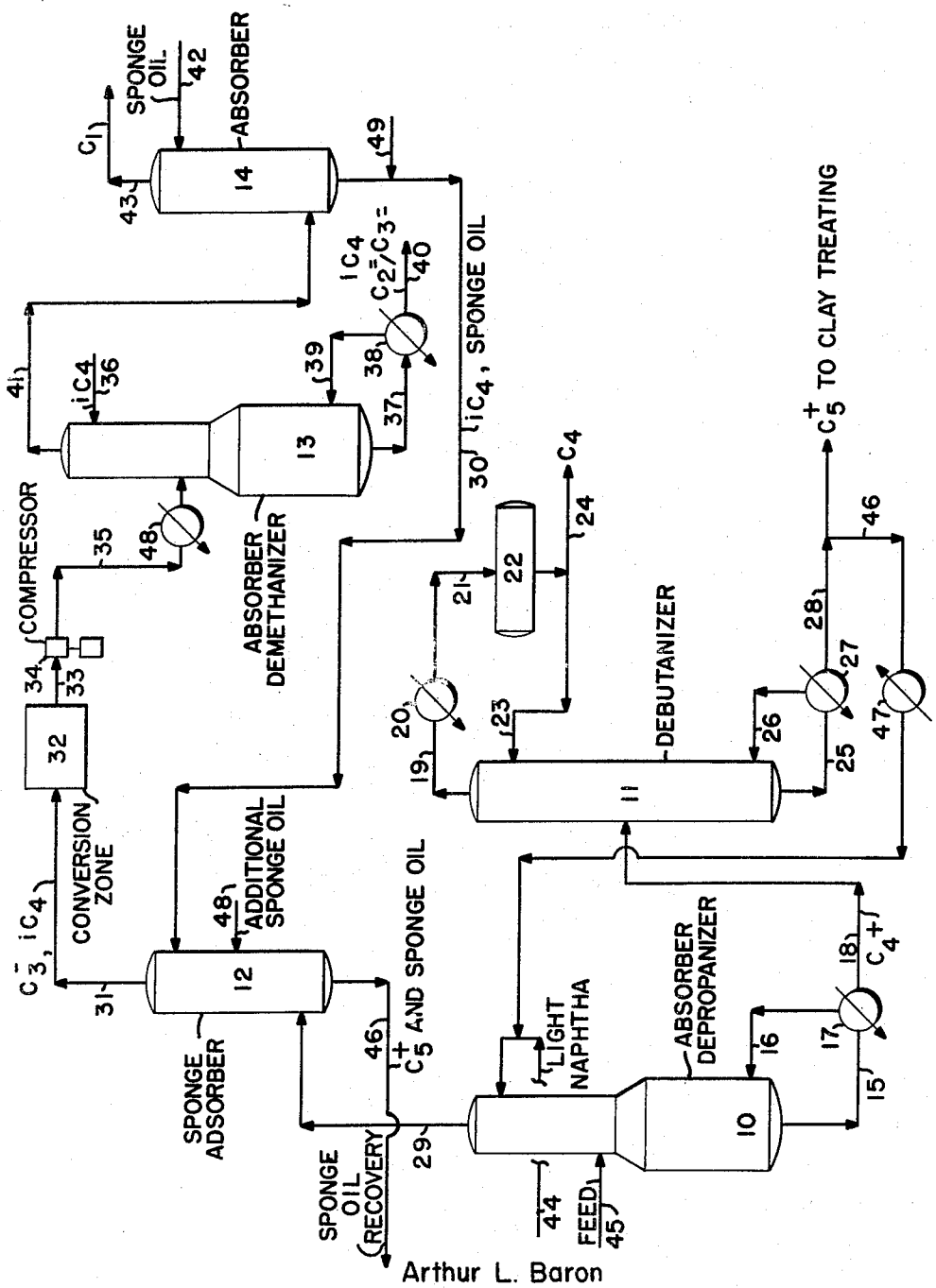
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LIGHT ENDS ABSORPTION SYSTEM

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LIGHT ENDS ABSORPTION SYSTEM

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The present invention is concerned with the recovery of light end fractions of a hydrocarbon conversion system. More particularly, it deals with an improved method of utilizing isobutane as a lean oil stream in the recovery of light products from a steam cracking reaction.

Various hydrocarbon processes yielding a variety of C_1 to C_{10} hydrocarbons are well known in the art. Separation of products often proves to be a difficult, as well as an expensive, operation. This is particularly so when treating the effluent of a steam cracking reaction zone. Steam cracking reactions give a spectrum of products ranging all the way from H_2, methane, ethylene and ethane to much higher molecular weight olefins, diolefins and aromatics.

Heretofore, when it was desired to recover ethylene and/or propylene product from the light ends of the steam cracker effluent, it was customary to pass at least a portion of the steam-cracked product into a primary separation zone operating under conditions adjusted so as to essentially remove C_4 and heavier constituents from its overhead, which then consisted primarily of ethane, ethylene, propane and propylene, and hydrogen, methane diluent. However, since light cracked naphthas are conventionally employed as feed to the top portion of the separation zone so as to scrub out butane and C_5 and higher constituents, the overhead of the separation zone invariably contains some unsaturated C_5^+ impurities which must be removed prior to the purification and recovery of the ethylene and/or propylene. Conventionally, this was normally accomplished by a complete sponge oil circuit about a C_5^+ impurities removal zone, ie. sponge oil absorbing C_5^+ materials, followed by separating the sponge oil from absorbed C_5^+ and directly re-using the sponge oil to scrub additional separation zone overheads.

It is further known in the prior art to employ isobutane as a lean oil in recovering ethylene and/or propylene from the light ends stream after removal of C_5^+ constituents. Light gases are withdrawn overhead while an isobutane-ethylene/propylene stream is withdrawn as bottoms. This latter step is advantageous in that since isobutane is a feed material for alkylation reactions, a recovered stream of it and ethylene and/or propylene can directly be used as the feed to an alkylation zone.

However, though considerable effort has gone into improving light ends systems, the methods described above suffer from important disadvantages. In order to prevent loss of isobutane, a valuable hydrocarbon, refrigeration was employed in the operations in which isobutane acted as a lean oil. Temperature control had to be accurately maintained. As is readily appreciated, the expenses of refrigeration as well as the difficulty of precise temperature control present distinct liabilities.

In cases where sponge oil was used to recover isobutane gases which may have passed overhead with light gases, considerable operating and investment cost was incurred due to this second sponge oil circuit required in the overhead system. A combination of an absorber and a stripping or other sponge oil recovery zone was employed in effecting the absorption treatment of each hydrocarbon stream.

In accordance with the present invention, isobutane may readily be used to recover light ends without incurring the above-described difficulties. Application of isobutane as an absorption oil is combined with the removal of C_5^+ constituents from the light ends recovery system in a manner yielding a highly efficient operation, little or no loss of isobutane, and reduced operating and investment costs.

More particularly, the light ends treating zone (normally an absorber-demethanizer) to which isobutane is fed is operated with little or no refrigeration so as to allow a minor but appreciable amount of the isobutane to go overhead with the light gases. The isobutane thus vaporized may be 5–10 mol percent of the light gas overhead. The isobutane-containing overhead is then contacted with a sponge oil having an atmospheric boiling point of at least 200–400° F., isobutane being absorbed in the sponge oil while light gases (H_2, C_1 and residual C_2's) are taken overhead. The mixture of sponge oil and isobutane is then employed to treat the overhead of the primary separation zone (for example, an absorber-depropanizer), C_5^+ constituents being thus removed in the sponge oil while the isobutane is simultaneously stripped out and returned to the subsequent light ends treating steps, e.g. the absorber-demethanizer, which uses isobutane lean oil, as mentioned before.

By operating in this manner, precise temperature control over the step in which the isobutane serves as a lean oil is not required. No separate stripping operation is needed to recover isobutane since isobutane is returned to the light ends system in the same operation in which the sponge oil removes C_5^+ impurities.

It should clearly be noted that the present specific method of operation offers considerably more advantage than one in which the sponge oil-absorbed isobutane mixture is sent to the steam cracker quench or a primary fractionation tower or to the primary separation zone. In that event, the isobutane would be lost to the C_4 cut produced in the steam cracking operation, thereby diluting the C_4 cut as well as increasing the isobutane loss. Further, presence of isobutane in the steam cracked C_4 cut is undesirable for subsequent butadiene extraction and butene utilization.

By way of clarifying nomenclature, the expression "less than C_4 constituents" (used in describing the major portion of the primary separation zone overhead to be treated by the present invention) indicates the substantial absence of butane, butenes, butadiene, etc. It may denote streams containing C_3 materials, or streams wherein the only light hydrocarbons present in substantial amounts contain two or less carbon atoms.

The term "sponge oil" denotes an absorber oil of higher boiling range-lower vapor pressure than the original lean oil, the vaporized portion of which it serves to absorb.

The various aspects of the present invention will be made more clearly apparent by reference to the following description, drawing and accompanying specific embodiment.

Referring to the drawing, shown therein is a light ends recovery system operating in accordance with the present invention and comprising basically units **10** through **15**. Initially it is to be noted that units **10** and **11** and associated facilities, i.e. the C_4 and heavier recovery system, operate substantially in a conventional manner but have been included for the benefit of overall clarity of presentation.

Steam cracking, per se, is well known in the art and thus need not be described in detail. Suffice to note that typically a naphtha or gas oil hydrocarbon is cracked

at temperature of 1200 to 1500° F. and in the presence of 5 to 40 wt. percent steam (based on hydrocarbon feed) to yield saturated and unsaturated products, a considerable portion of which comprise C_1 to C_4 hydrocarbons.

After being subjected to quenching in a quench or fractionation tower, steam cracker effluent is compressed and introduced into a primary separation zone, absorber **10**, by means of inlet **45**.

In the embodiment described, unit **10** operates as an absorber-depropanizer. Light naphtha, e.g. boiling between C_5 to 430° F., and generally derived from steam cracking, is introduced into the upper portion of depropanizer **10** by line **44**. The C_4 and C_5^+ constituents of the steam cracker effluent are absorbed in the downflowing oil, which is withdrawn from the unit by line **15**. A portion of the resulting fat oil is heated by reboiler **17** or the like and recycled by line **16** to unit **10** in order to strip out absorbed C_3 and lighter hydrocarbons from the bottoms product. Absorption can be carried out at a temperature of 35 to 120° F., and a pressure in the range of 100 to 300 p.s.i.g. is employed.

Fat oil containing C_4^+ materials is passed by line **18** to a conventional debutanizer **11** wherein C_5^+ constituents are removed as bottoms through line **25** and the C_4's taken overhead through exit **19**. Overhead C_4 gases are cooled to a liquid in condenser **20**, condensate being passed to reflux drum **22** by line **21**. A portion of the condensate is refluxed to unit **11** by line **23** and the product composed substantially only of C_4 compounds withdrawn by line **24**. This C_4 stream may then be sent to cuprous ammonium acetate extraction for the recovery of butadiene or otherwise processed.

Debutanizer bottoms are withdrawn by line **25**, heated in unit **27** and a portion thereof recycled by conduit **26** in order to strip C_4 and lighter materials out of the bottom product. Typically, the tower operates at a temperature in the range of 135 to 245° F. The fat oil stream recovered through outlet **28** consists essentially of C_5 and higher hydrocarbons, and is generally passed to other units for chemicals recovery or work-up for inclusion in the gasoline pool. A portion of this stream may be used on the lean oil in absorber-depropanizer **10**, as shown by line **46** via cooler **47**.

As previously noted, the system described up to this point is generally well known in the art.

The overhead of unit **10** passing through line **29** is composed principally of less than C_4 constituents, e.g. ethane, ethylene, propane, propylene, along with hydrogen, methane and some acetylenes and propadiene. Due to the vaporization of the light lean oil used in absorber **10**, this overhead stream will also contain about 1 to 5, e.g. 2.5 mol percent of C_5^+ materials, which may be termed to be impurities with respect to the light ends overhead, and are undesirable in the subsequent processing steps.

Thus, in addition to separately recovering various light hydrocarbons from the overhead, it is necessary to remove these C_5^+ materials. The present invention advantageously serves to accomplish both these steps.

Holding in abeyance the means by which these C_5^+ impurities are removed (which will be later described in detail), after their removal, the light ends stream is sent to various recovery and conversion zones. In typical cases wherein acetylenes are present in the light overhead, the C_3^- stream is passed through conduit **31** to an acetylene conversion zone **32**. This generally takes the form of a conventional mild catalytic hydrogenation, the purpose of which is to convert acetylene into ethylene, and propadiene and methyl acetylene into propylene without saturating olefins present in the gas stream. For the purposes of illustration, the hydrocarbons are reacted at a temperature of 350 to 600° F. (depending on catalyst age), at a pressure of 100 to 300 p.s.i.g., e.g. 200 p.s.i.g., and in the presence of a cobalt molybdate or Cr-Ni-Co catalyst. The hydrogen steam cracking product present in the gas stream is usually more than sufficient to provide necessary hydrogen for treating the minor quantities of acetylenes and diolefin.

The thus treated stream is withdrawn through exit **33**. In most situations, it is then desired to separate out the C_1 and lighter materials from the C_2/C_3 constituents which are suitable for feed to an alkylation unit. This is done by means of absorber demethanizer **13**.

In order to bring the light hydrocarbon effluent of unit **32** to proper conditions for demethanization, they are circulated to compressor **34** by line **33**. The compressor serves to raise the pressure of the hydrocarbon stream to the level of demethanizer **13**. The compression effluent stream in line **35** is then cooled in cooler **48** to condense out water and to reduce the temperature of the hydrocarbon to the temperature of the demethanizer.

As is appreciated by the art, isobutane may be advantageously used as a lean oil in the absorber demethanizer. Whereas in the prior art operating conditions were normally adjusted so as to prevent any vaporization of isobutane lean oil, i.e. refrigeration was applied to maintain a demethanization temperature of 0 to 60° F. at 400 to 700 p.s.i.g. pressure, in accordance with the present invention, refrigeration and the necessity of drying the feed to the absorber-demethanizer to prevent ice formation etc. can be substantially eliminated. Absorber-demethanizer **13** is operated at about 75 to 120° F. top temperature and 120 to 170° F. bottoms temperature (400 to 700 p.s.i.g.), thus allowing a minor fraction of the isobutane fed thereto through line **36** to be taken overhead through line **41** while the bulk of the isobutane absorbs C_2 and C_3 constituents, e.g. ethylene and propylene, and is withdrawn from unit **13** by line **37**. In the system illustrated, unit **13** is at 600 p.s.i.g. with an 85° F. top and 145° F. bottoms temperature. Generally, 2 to 10%, e.g. 5%, of the isobutane lean oil will be vaporized and taken overhead.

In the embodiment illustrated, isobutane introduced by line **36** is at a temperature of 85° F. and the light ends of line **35** are at 85° F. About 0.5 to 2.0, e.g. 1.3 mols of isobutane are introduced into the demethanizer for each mol of light ends being fed through line **35**.

Normally, at least a portion of the isobutane fat oil, after reboiling in auxiliary reboiler **38**, is recirculated to demethanizer **13** by line **39** in order to strip out methane and hydrogen from the bottoms product. The stream withdrawn through exit **40** contains isobutane along with ethylene and propylene and smaller amounts of ethane and propane, and is normally employed as a feed to an alkylation process.

The light ends taken overhead through line **41**, containing methane and hydrogen along with the vaporized isobutane, are then passed to absorber **14**. Introduced into the upper portion of the absorber through inlet **42** is a sponge oil having a minimum initial boiling point of at least about 200° F. (at atmospheric pressure). The sponge oil may conveniently be a heavy naphtha, kerosene, or light gas oil.

Absorber **14** operates at a temperature of 75 to 120° F. and a pressure in the range of 400 to 700 p.s.i.g. In the embodiment described, it is operated at 85° F. and 600 p.s.i.g., about 0.2 to 0.4 mol, e.g. 0.25 mol, of sponge oil (a 280/360° F.V.T., degree Fahrenheit vapor temperature, oil stream) being used per mol of gases in line **41**. The quantity of sponge oil will normally be somewhat in excess of that theoretically required to recover the isobutane since the high value of isobutane requires its complete recovery be attempted, and the sponge oil is to additionally serve as an absorption medium in unit **12**. Of course, additional quantities of sponge oil may be added to line **30**, by means of line **49** or by means not shown, to supplement the quantity of absorption medium available for absorber **12**.

Methane and hydrogen are taken overhead through line **43** while the sponge oil-isobutane mixture is circulated through line **30** to sponge absorber **12** wherein it is contacted with the overhead of absorber depropanizer **10**. Absorber **12** normally operates at 100 to 300 p.s.i.g. pressure and 80 to 120° F. temperature. In the present example it operates at 200 p.s.i.g. and 85° F. The sponge oil (having an atmospheric boiling point of at least 200° F.) serves to condense and absorb the C_5^+ constituents in the depropanizer overhead. Since the overhead of unit **10** has a temperature of at least 90° F. and the pressure of absorber **12** is at most 300 p.s.i.g., isobutane present in the sponge oil is simultaneously stripped out of the mixture of line **30**, and is recovered in the overhead of the absorber along with C_3^- and hydrogen. If desired, additional sponge oil may be added by line **48**. Generally, 0.2 to 0.4 mol sponge oil mixture, e.g. 0.25 mol, is employed per mol of unit **10** overhead.

The isobutane taken from the demethanizer overhead is thus recovered in the same step in which undesired C_5^+ constituents are removed. The isobutane is circulated through line **31** along with the light ends to the processing steps previously described, ultimately finding its way back to treating zone **13** for further use therein.

Sponge oil containing C_5^+ impurities is withdrawn from absorber **12** through line **46**. Sponge oil may be recovered for further absorption of isobutane by passing the C_5^+-sponge oil mixture to the stream cracking quench tower, to a separate stripping zone or by other means readily apparent to those skilled in the art.

Table 1 indicates the principal components found in the various streams described above.

TABLE 1

Stream compositions

Reference Numeral in Drawing	44	45	29	18	31	41	40	43	30	46
H_2	----	x	x	----	x	x	----	x	----	----
CH_4	----	x	x	----	x	x	----	x	----	----
C_2H_4	----	x	x	----	x	----	x	----	----	----
C_2H_6	----	x	x	----	x	----	x	----	----	----
C_3H_6	----	x	x	----	x	----	x	----	----	----
C_3H_8	----	x	x	----	x	----	x	----	----	----
C_4H_8	----	x	----	x	----	----	----	----	----	----
i-C_4H_{10}	----	x	----	x	x	x	x	----	x	----
n-C_4H_{10}	----	x	----	x	----	----	----	----	----	----
C_5 and heavier	x	x	x	x	----	----	----	----	x	x

Tabulated below is a compilation of data applicable to the practice of the present invention.

TABLE 2

	Broad Range	Preferred Range
Fraction of Isobutane Feed to Unit 13 Vaporized into Overhead, Percent	2 to 10	4 to 6
Minimum Initial Boiling Point of Sponge Oil, ° F	200 to 400	250 to 350
Isobutane Overhead Absorption Zone (Unit 14):		
Temperature, ° F	75 to 120	80 to 90
Pressure, p.s.i.g	400 to 700	450 to 650
C_5^+ Sponge Absorber (Unit 12):		
Temperature, ° F	80 to 120	80 to 100
Pressure, p.s.i.g	100 to 300	150 to 250

Various modifications may be made to the practice of the present invention. For example, the initial separation zone (unit **10**) may be an absorber de-ethanizer when ethylene rather than a propylene/ethylene mixture is desired for alkylation feed. Though the overhead in line **29** will not contain substantial portions of propylene, the isobutane-sponge oil-C_5^+ removal features will be substantially as previously described. In another modification, unit **13** may act as an alkylation reactor, isobutane and ethylene and/or propylene in the light overhead being reacted in the presence of an alkylation catalyst, e.g. aluminum chloride, under standard alkylation conditions. Methane and hydrogen wil pass through unit **13** substantially unconverted, while unreacted isobutane is recovered from the reaction unit overhead in the manner heretofore described. In its broadest aspects, the present invention may be employed in gas cracking, catalytic cracking, and other processes in addition to steam cracking, all these processes being related by their common problem of light ends recovery.

Having described the present invention, that which is sought to be protected is succinctly set forth in the appended claims.

What is claimed is:

1. In a process wherein an initial stream of relatively light hydrocarbons which contains some C_5 and higher constituents is to be separated into component fractions, wherein said C_5 and higher constituents are removed from said light hydrocarbons by absorption in an oil stream, and wherein isobutane is employed to contact said light hydrocarbons in a treating zone after removal of said C_5 and higher constituents, a minor portion of said isobutane passing overhead from said treating zone, the improved method of separating light hydrocarbons which comprises, contacting the overhead of said treating zone with a sponge oil having a boiling point of at least 200° F. so as to absorb isobutane in said sponge oil, thereafter contacting said sponge oil containing isobutane with said initial stream in an absorption zone so as to vaporize isobutane while absorbing C_5 and higher constituents, removing sponge oil containing C_5 and higher constituents from said absorption zone, and recovering isobutane and light hydrocarbons as the overhead of said absorption zone.

2. The process of claim 1 wherein said initial feed stream is derived from a steam cracking reaction zone, and said treating zone is an absorber-dimethanizer zone, a minor portion of said isobutane passing overhead along with methane.

3. The process of claim 1 wherein said sponge oil contacts the overhead of said treating zone at a temperature in the range of 75 to 120° F., and at a pressure of 400 to 700 p.s.i.g.

4. In recovering the light ends products of a steam cracking reaction wherein an initial hydrocarbon stream predominantly composed of less than C_4 constituents along with some C_5^+ impurities is to be separated into light ends fractions, wherein said C_5^+ impurities are removed by their absorption in an oil stream, and wherein said thus treated hydrocarbon stream is thereafter contacted with isobutane in an absorption zone, the improved method of recovering light ends fraction which comprises; operating said absorption zone so as to allow a minor portion of said isobutane to be withdrawn as part of the overhead of said absorption zone; contacting said absorption zone overhead with a sponge oil having an initial boiling point of at least 200° F. so as to absorb said minor portion of isobutane in said sponge oil; and passing said sponge oil and absorbed isobutane mixture to a C_5^+ removal zone wherein it contacts said initial hydrocarbon stream, said mixture serving to absorb C_5^+ impurities in said sponge oil while giving up isobutane to the light overhead stream of said C_5^+ removal zone.

5. The improved method of claim 1 wherein said absorption zone is an absorber-demethanizer zone and about 2 to 10% of the isobutane fed to said zone is vaporized as part of the overhead of said zone.

6. The improved method of claim 4 wherein said initial hydrocarbon stream comprises C_3, C_2 and C_1 constituents recovered from an absorber-depropanizer zone which has been used to treat steam cracking effluent.

7. The improved method of claim 4 wherein said initial hydrocarbon stream is composed primarily of C_2^- and C_5^+ constituents derived from an absorber de-ethanizer zone which has been used to treat steam cracking effluent.

8. In the process for recovery of light ends from a steam cracking zone wherein steam cracking zone effluent

is treated in an absorber-depropanizer zone, wherein the light ends overhead stream of said absorber-depropanizer zone comprises predominantly less than C_4 constituents along with some C_5^+ impurities, wherein said light ends stream is treated with an isobutane stream in an absorber-demethanizer zone after removal of C_5^+ impurities, the improvement which comprises; operating said absorber-demethanizer zone so as to permit about 2 to 10% of said isobutane stream to be withdrawn in the overhead stream of said absorber-demethanizer; contacting said overhead stream of said absorber-depropanizer with a sponge oil having an initial boiling point of 200° F. so as to absorb the isobutane of said stream; passing the resulting mixture of sponge oil and isobutane to a C_5^+ absorption zone, and contacting said mixture with the overhead of said absorber-depropanizer zone at temperatures of 80 to 120° F. and pressures of 100 to 300 p.s.i.g. so as to absorb C_5^+ impurities in said sponge oil while isobutane is freed from said mixture and is taken overhead along with said predominantly less than C_4 constituents for further treatment.

9. The improvement of claim 8 wherein the overhead stream of said absorber-demethanizer is contacted with said sponge oil at a temperature of 75 to 120° F., and a pressure within the range of 400 to 700 p.s.i.g.

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