Gasification

Presented

By

Robert (Bud) Klepper

Gasification

♦ The manufacture of combustible gases from solid fuels is an ancient art, but by no means a forgotten one.

♦ The term gasification covers the conversion of any carbonaceous fuel to a gaseous product with a useable heating value. This definition excludes combustion.

Biomass Gasification

History and Development

- 1620 To 1720 Fuel Wood Shortage Resulted in Drop in Iron Production, from 180,000 Tons to 18,000 Tons Per Year.
- 1669 Thomas Shirley Conducted Crude Experiments with Carbonated Hydrogen.
- 1699 Dean Clayton Obtained Coal Gas from Pyrolitic Experiment.
- 1788 Robert Gardner Obtained the First Patent with Regard to Gasification.
- 1792 First Confirmed Use of Producer Gas Reported, Murdoc Used the Gas Generated from Coal to Light a Room in His House. For Many Years After Coal Gas was Used for Heating and Cooking.
- 1801 Lampodium Proved the Possibility of using Waste Gases Escaping from the Charring of Wood.
- 1804 Fourcroy Found the Water Gas by Reaction of Water with a Hot Carbon.

History and Development Continued

- 1812 The Development of the First Gas Producer which uses Oil as Fuel.
- 1840 The First Commercially Used Gasifier was Built in France.
- 1861 Real Breakthrough in Technology with introduction of Siemens Gasifier. This Gasifier is Considered to be the First Successful Unit.
- 1878 Gasifiers were Successfully Used with Engines for Power Generation.
- 1900 The First 600 Horsepower Gasifier was Exhibited in Paris. Thereafter, Larger Engines up to 5400 Horsepower were put into Service.
- 1901 J.W. Parker Runs a Passenger Vehicle with Producer Gas.
- 1901-1920 Many Gasifier-Engine Systems were sold and used for Power and Electricity Generation. Until this Period all Processes Involving Coal were Cyclical.
- 1920 Carl Von Linde Commercialized the Cryogenic Separation of Air. This Allowed the First Fully Continuous Gasification Process.
- 1926 Winkler Fluid Bed Process.
- 1930 Nazi Germany Accelerated Effort to Convert Existing Vehicles to Producer Gas Drive as part of a Plan for National Security and Independence from Imported Oil.

History and Development Continued

- 1930 Began Development for Small Automotive and Portable Gas Producer. The British and French Governments Felt that Automotive Charcoal Gas Producer is more suitable for their colonies where supplies of Gasoline were Scarce and Wood that could be Charred to Charcoal was readily available.
- 1931 Lurgi Moving Bed Pressurized Process.
- 1939 About 250,000 Vehicles were registered in Sweden. Of those 90% were converted to producer gas drive. Almost all of the 20,000 tractors were operated on producer gas. 40% of the Fuel was Wood and the Remainder Charcoal.

History and Development Continued

♦ 1940 Koppers – Totzek Entrained Flow

♦ 1945 After the End of World War II, with Plentiful Gasoline and Diesel Available at Low Cost, Gasification Technology Lost its Glory and Importance.

♦ 1950 – 1969 During these Decades, Gasification was a Forgotten Technology. Many Governments in Europe believed that consumption of Wood at the Prevailing Rate would Reduce the Forests, Creating Several Environmental Problems.

♦1970 The 1970's Brought a Renewed Interest in the Technology for Power Generation in Small Scale. Since then Work is also Concentrated to use fuels other than Wood and Charcoal.

♦ 1974 Oil Embargo.

Gas Production

Until the end of the 1920s the only gases that could be produced in a continuous process were blast furnace gas and producer gas. Producer gas was obtained by partial oxidation of coke with humidified air. However, both gases have a low heating value (3,500 – 6,000 kj/m$_3$, or low Btu gas) and could therefore only be used in the immediate vicinity of their production.

The success of the production of gases from solids, can be attributed to the fact that gas is easier to handle than a solid fuel. There is also a more basic chemical reason that can best be illustrated by the following reactions:

$$C + \tfrac{1}{2} O_2 = CO \qquad -\ 111\,MJ/kmol$$

$$CO + \tfrac{1}{2} O_2 = CO_2 \qquad -\ 283\,MJ/kmol$$

$$C + O_2 = CO_2 \qquad -\ 394\ MJ/kmol$$

Gas Production Continued

These reactions show that by " investing" 28% of the heating value of pure carbon in the conversion of the solid carbon into the gas CO, 72% of the heating value of the carbon is conserved in the gas. In practice, the fuel will contain not only carbon but also some hydrogen, and the percentage of the heat in the original fuel, which becomes available in the gas. Modern processes yield between 75 and 88% .

Although gasification started as a source for lighting and heating from 1900 onwards the water gas process, which produced a gas consisting of about equal amounts of hydrogen and carbon monoxide, also started to become important for the chemical industry. The endothermic water gas reaction can be written as:

$$C + H_2O \leftrightarrow CO + H_2 \quad +131 MJ/kmol$$

By converting part or all of the carbon monoxide into hydrogen following the CO shift reaction.

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad +41 MJ/kmol$$

It became possible to convert the water gas into hydrogen or synthesis gas (a mixture of H2 and CO) for ammonia and alcohols synthesis.

It was only after Carl Von Linde commercialized the cryogenic separation of air during the 1920s that fully continuous gasification processes using an oxygen blast became available for the production of synthesis gas and hydrogen. This was the time of the development of some of the important processes that were the forerunners of many of today's units: The Winkler Fluid Bed Process (1926), The Lurgi Moving Bed Pressurized Gasification Process (1931), The Koppers-Totzek Entrained Flow Process (1940s).

With the establishment of these processes little further technological progress in the gasification of solid fuels took place over the following forty years. Nonetheless, capacity with these new technologies expanded steadily, playing their role partly in Germany's wartime synthetic fuels program and on a wider basis in the worldwide development of the ammonia industry

Reactions

During the process of gasification of solid carbon whether in the form of coal, coke, or car the principle chemical reactions are those involving carbon, carbon monoxide, carbon dioxide, hydrogen, water (or steam), and methane these are :

Combustion reactions,

$$C + \frac{1}{2} O_2 = CO \qquad - 111 \mathrm{MJ/kmol}$$

$$CO + \frac{1}{2} O_2 = CO_2 \qquad - 283 \mathrm{MJ/kmol}$$

$$H_2 + \frac{1}{2} O_2 = H_2O \qquad -242 \mathrm{MJ/kmol}$$

The Boudourard reaction,

$$C + CO_2 \leftrightarrow 2\,CO \qquad +172 \mathrm{MJ/kmol}$$

The Water Gas reaction,

$$C + H_2O \leftrightarrow CO + H_2 \qquad +131 \mathrm{MJ/kmol}$$

The Methanation reaction,

$$C + 2\,H_2 \leftrightarrow CH_4 \qquad - 75 \mathrm{MJ/kmol}$$

As reactions with free oxygen are all essentially complete under gasification conditions, combustion reactions do not need to be considered in determining an equilibrium syngas composition. The three heterogeneous (i.e., gas and solid phase) Boudouard, Water Gas and the Methanation reactions are sufficient.

Reactions Continued

In general, we are concerned with situations where also the carbon conversion is essentially complete. Under these circumstances we can reduce Boudouard, Water Gas and Methanation reactions to the following two homogeneous gas reactions:

CO shift reaction:

$CO + H2O \leftrightarrow CO2 + H2$ -41MJ/kmol

The Steam Methane Reforming reaction:

$CH4 + H2O \leftrightarrow CO2 + 3H2$ +206MJ/kmol

Gas Producers (Gasifiers)

Gas producers are classified according to how oxidization is introduced in the fuel column History of gasification reveals several designs of gasifiers. The most commonly built gasifiers are classified as:

♦ **Updraft Gas Producer**

♦ **Downdraft Gas Producer**

♦ **Twin-Fire Gas Producer**

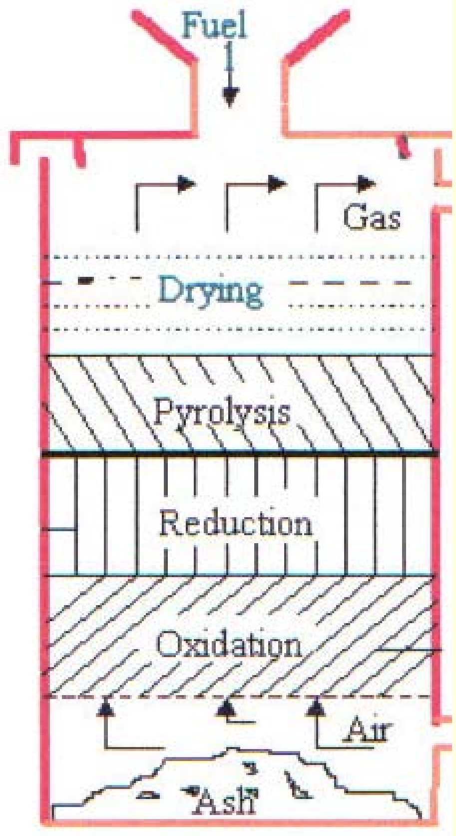
♦ **Cross draft Gas Producer**

♦ **Other Gas Producer**

Gasifiers

Updraft Gas Producer

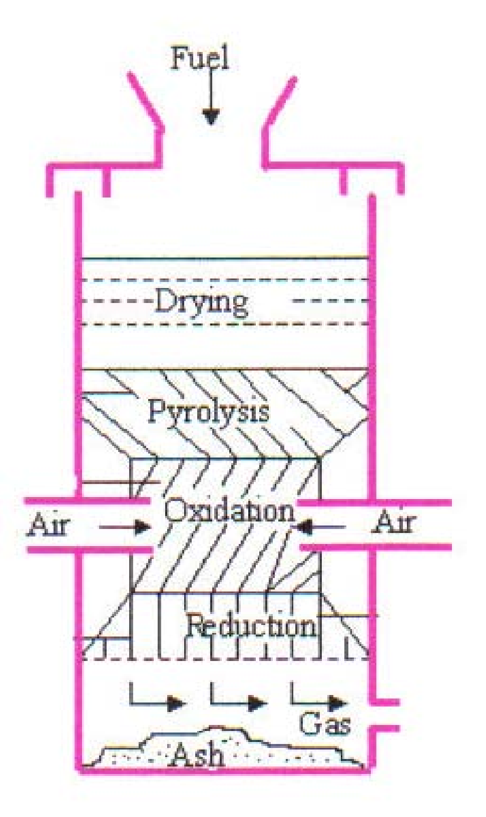
An Updraft Gasifier has clearly defined zones for partial combustion, reduction, and Pyrolysis. Air or oxygen is introduced at the bottom and act as countercurrent to fuel flow. The gas is drawn at higher location. The Updraft gasifier achieves the highest efficiency as the hot gas passes through fuel bed and leaves the gaifier at low temperature. The sensible heat given by gas is used to preheat and dry fuel. The Disadvantages of updraft gasifiers are the excessive amount of tar in raw gas and poor loading capability.



Gasifiers Continued

Downdraft Gasifier

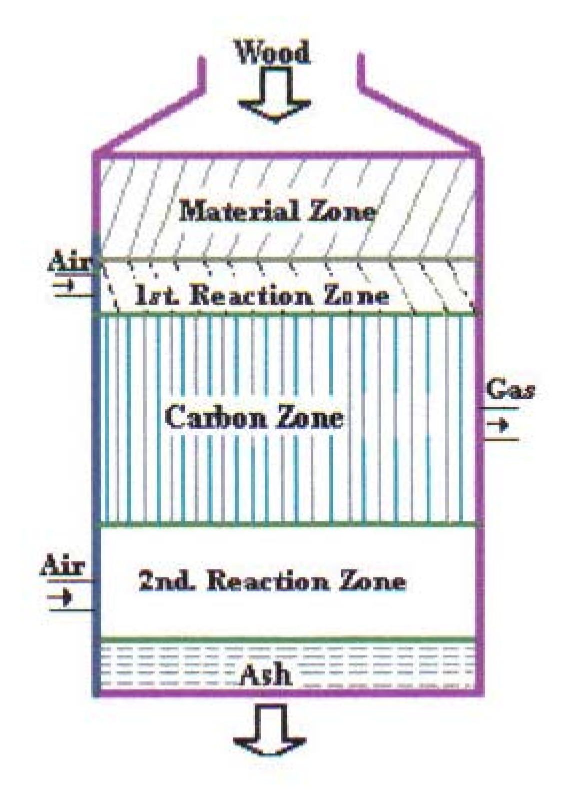
In the updraft gasifier, gas leaves the gasifier with high tar vapor which may seriously interfere the operation of internal combustion engine. This problem is minimized in the Downdraft gasifier. In this type, air or oxygen is introduced into downward flowing packed bed or solid fuels and gas is drawn off at the bottom. A lower overall efficiency and difficulties in handling higher moisture and ash content are common problems in small downdraft gas producers. The time (20-30 minutes) needed to ignite and bring plant to working temperature with good gas quality is shorter than Updraft gasifier. This gasifier is preferred to Updraft gasifier for internal combustion engines



Gasifiers Continued

Twin-Fire Gasifier

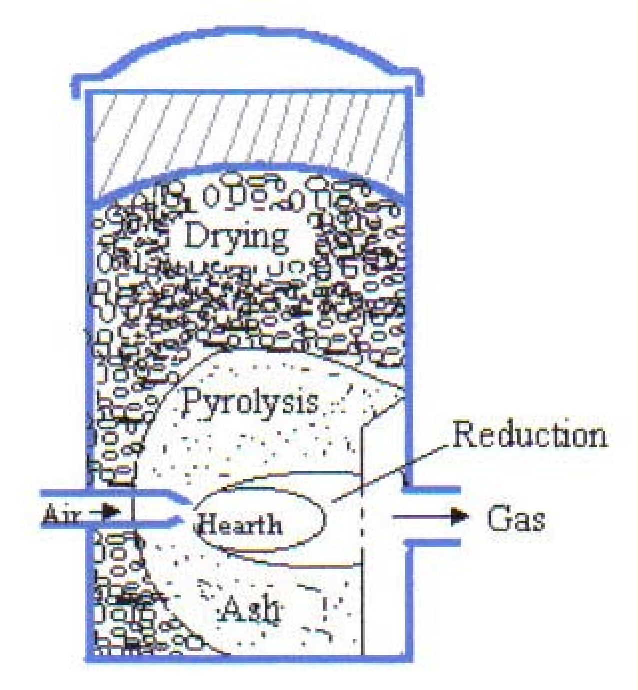
The advantage of co-current and counter-current gasifiers are combined in a so called Twin-Fire Gasifier. It consists of two defined reaction zones. Drying, low-temperature carbonization, and cracking of gases occur in the upper zone, while permanent gasification of charcoal takes place in the lower zone. The gas temperature lies between 460 to 520° C. Total process takes place with under pressure of -30mbar. Twin-Fire Gasifiers produce fairly clean gas.



Gasifiers Continued

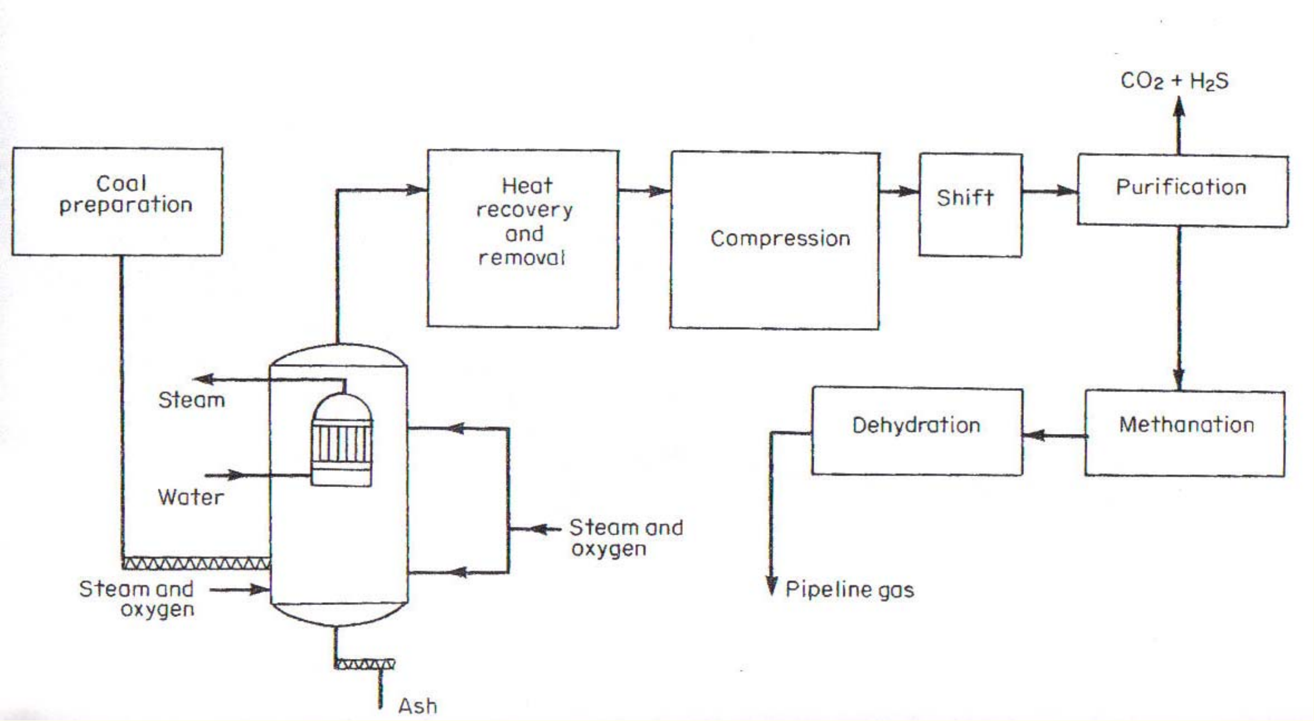
Crossdraft Gasifier

Crossdraft gasifiers, although they have certain advantages over updraft and downdraft gasifiers, they are not of ideal type. The disadvantages such as high exit gas temperature, Poor CO_2 reduction and high gas velocity are the consequence of the design. unlike downdraft and updraft gasifiers, the ash bin, fire and reduction zone in crossdraft gasifiers are separated. This design characteristics limit the type of fuel for operation to low ash fuels such as wood, charcoal, and coke. The load following ability of crossdraft gasifier is quite good due to concentrated partial zones which operates at temperatures up to 2000° C Start up time (5-10 minutes) is much faster than that of downdraft and updraft units. The relatively higher temperature in crossdraft gasifier has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used. Crossdraft gasifier operates well on dry blast and dry fuel.



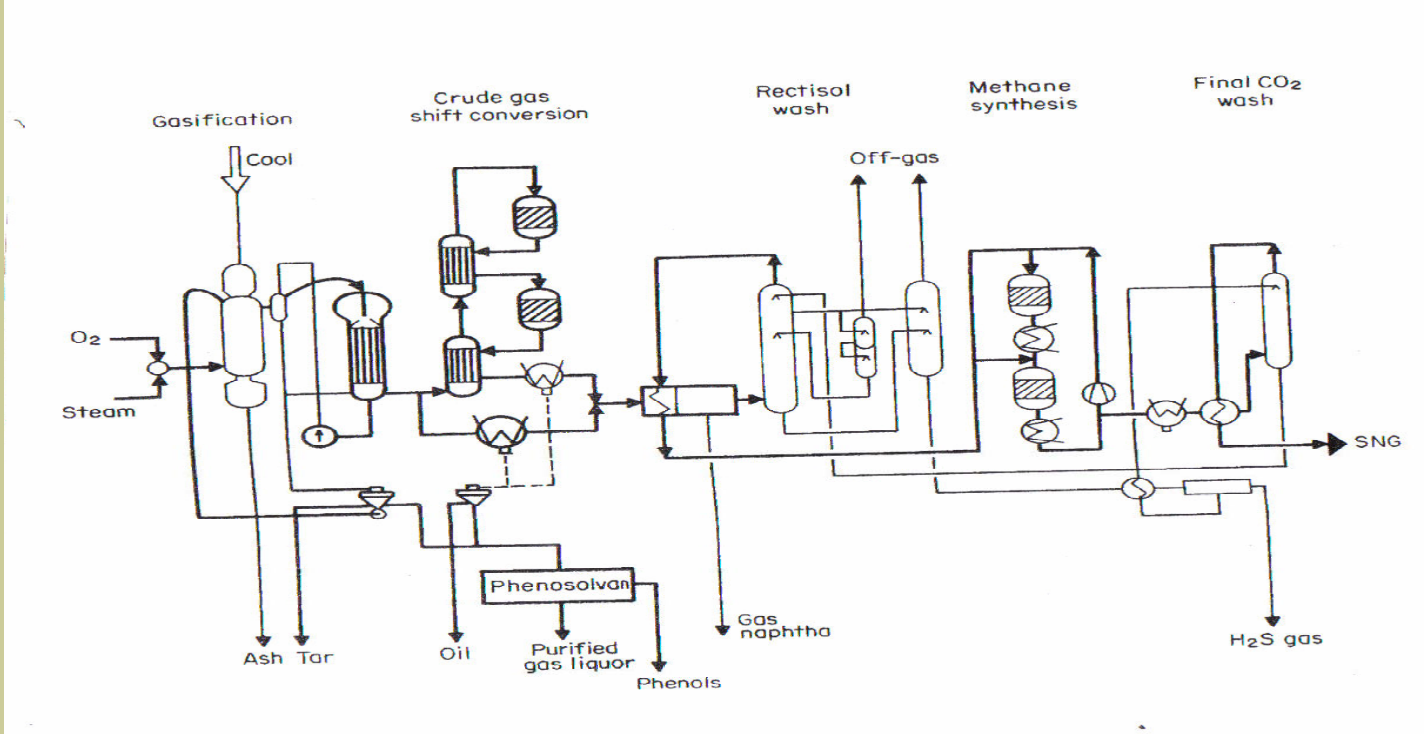
Gasifiers

Winkler



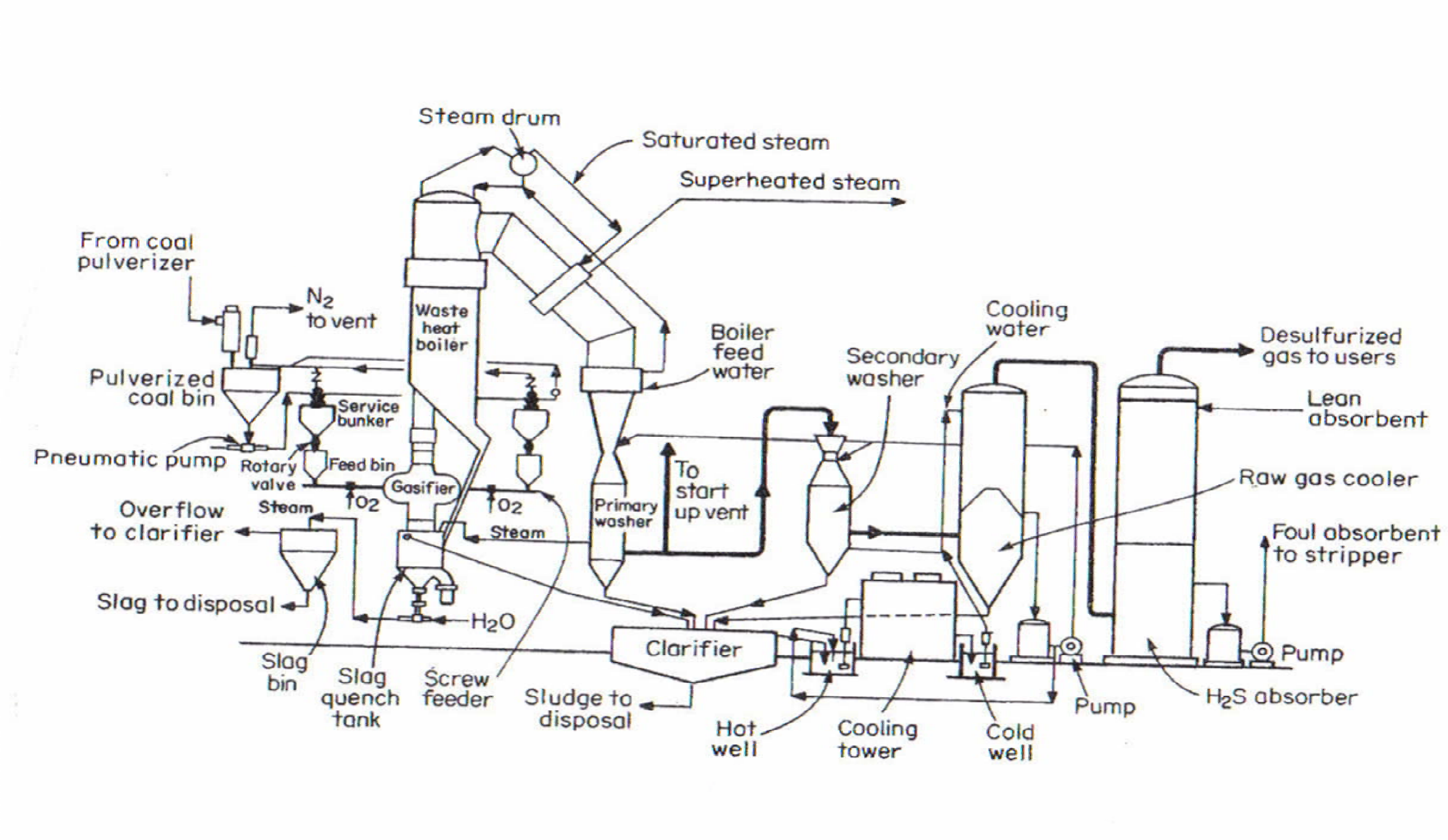
Gasifiers

Lurgi

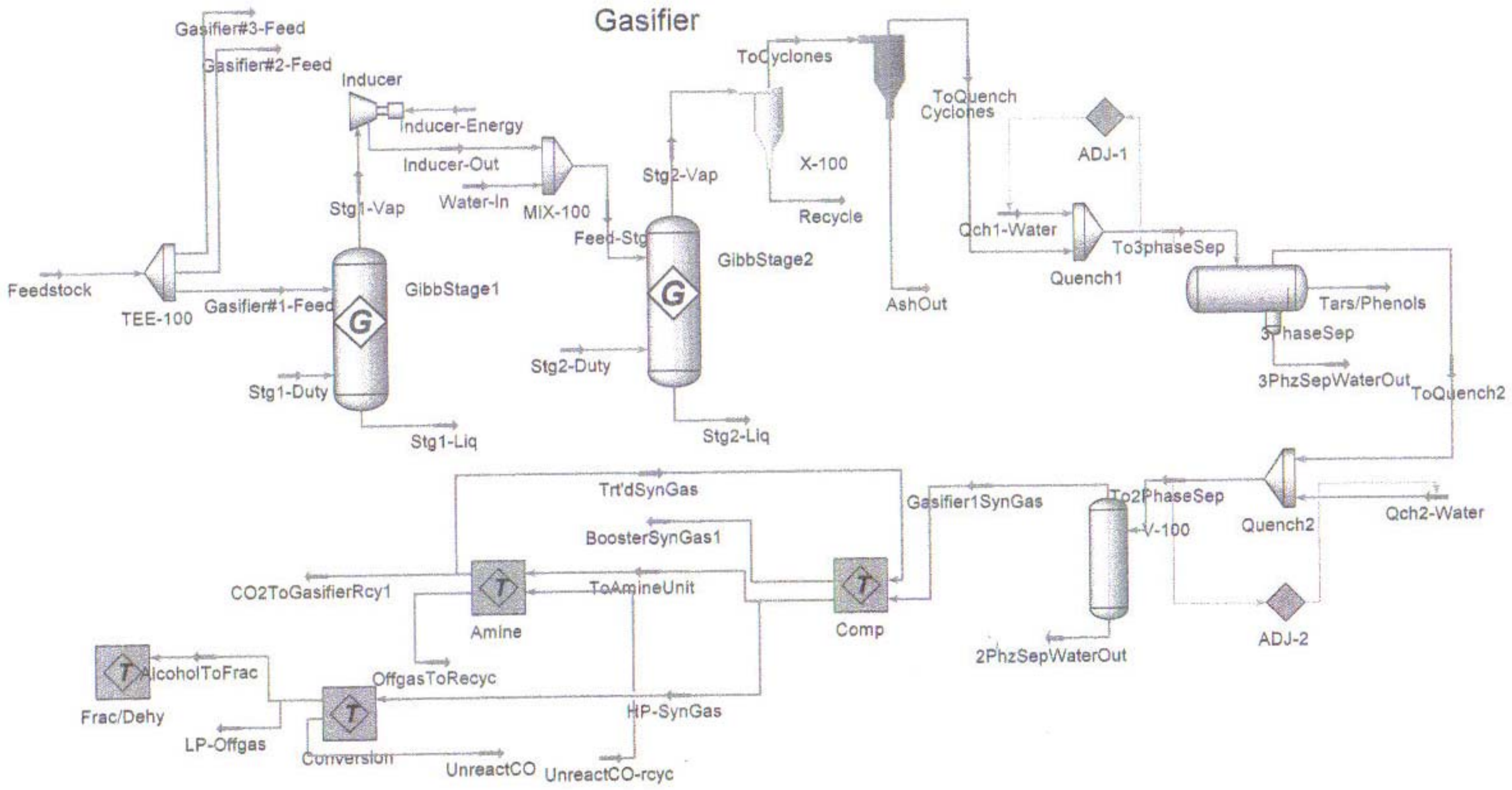


Gasifiers

Koppers-Totzek



BioConversion Technology PSRG Gasifier



Alcohol Synthesis

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BioConversion Technology
Alcohol Synthesis

The conversion of CO and H2 into various forms of Alcohol is well established within the chemical processing industries. The modern form of the industry was ushered in following the introduction, in 1923, by BASF of the first commercial process to synthesize methanol and higher alcohols from carbon monoxide and hydrogen.

The process was the product of the continuing research into the hydrogenation of carbon monoxide. This process had shown that depending upon the catalyst used and the process conditions employed, various alcohols could be produced. Fischer and Tropsch subsequent efforts in the 1930s, led to the development of processes for the manufacture of synthetic fuels.

Alcohol Synthesis

The Fischer Tropsch classes of catalyst facilitate through CO insertations, a chain building reaction, to produce long chain hydrocarbons. The following reaction are involved in the production of Methanol.

$\mathbf{CO + 2H_2 \qquad CH_3OH}$ The desired

$\mathbf{CO_2 + 3H_2 \qquad CH_3OH + H_2O}$

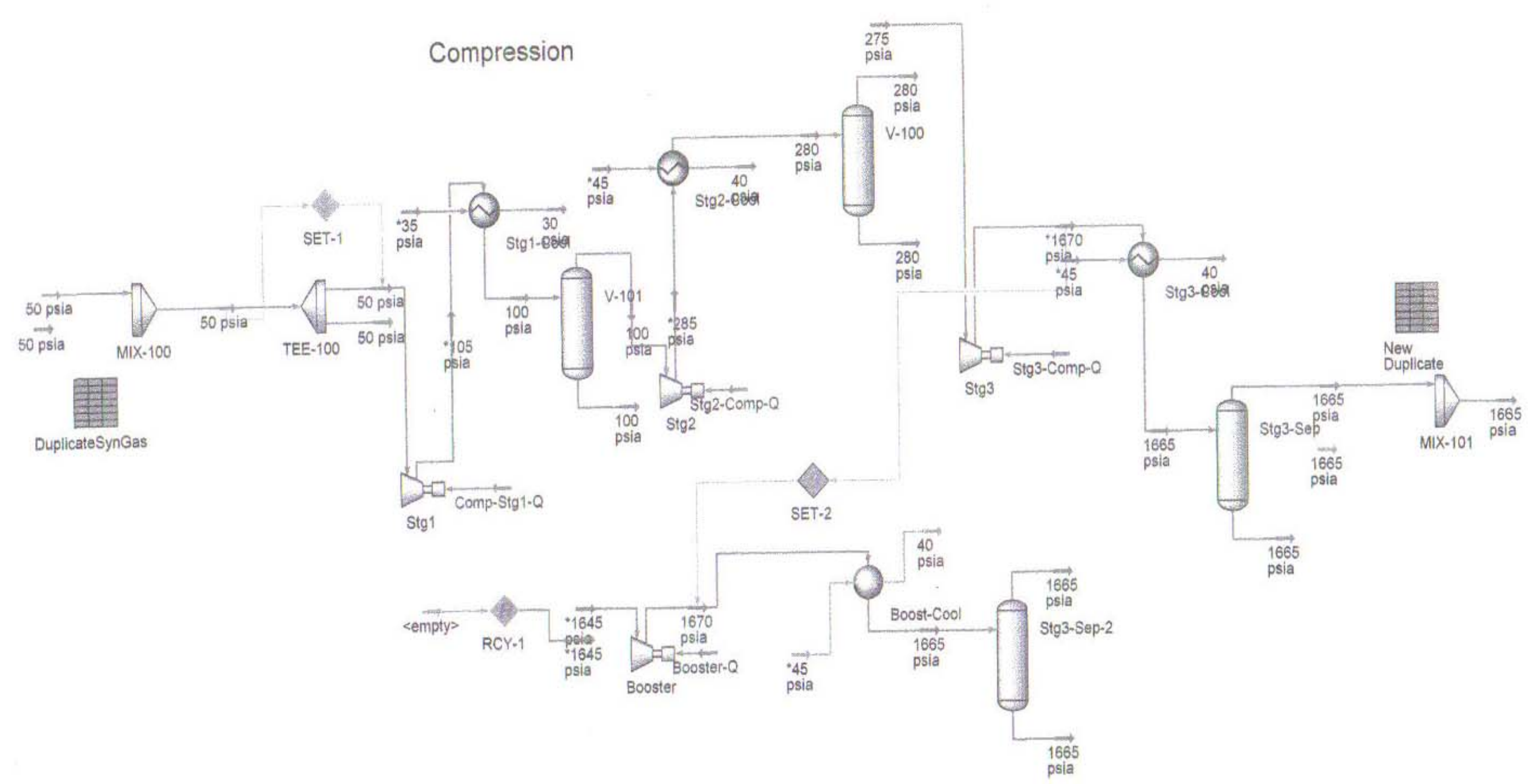
Alcohol Synthesis

In a Fischer Tropsch class of catalyst, the CO insertion continues to produce higher alcohols by the overall reaction.

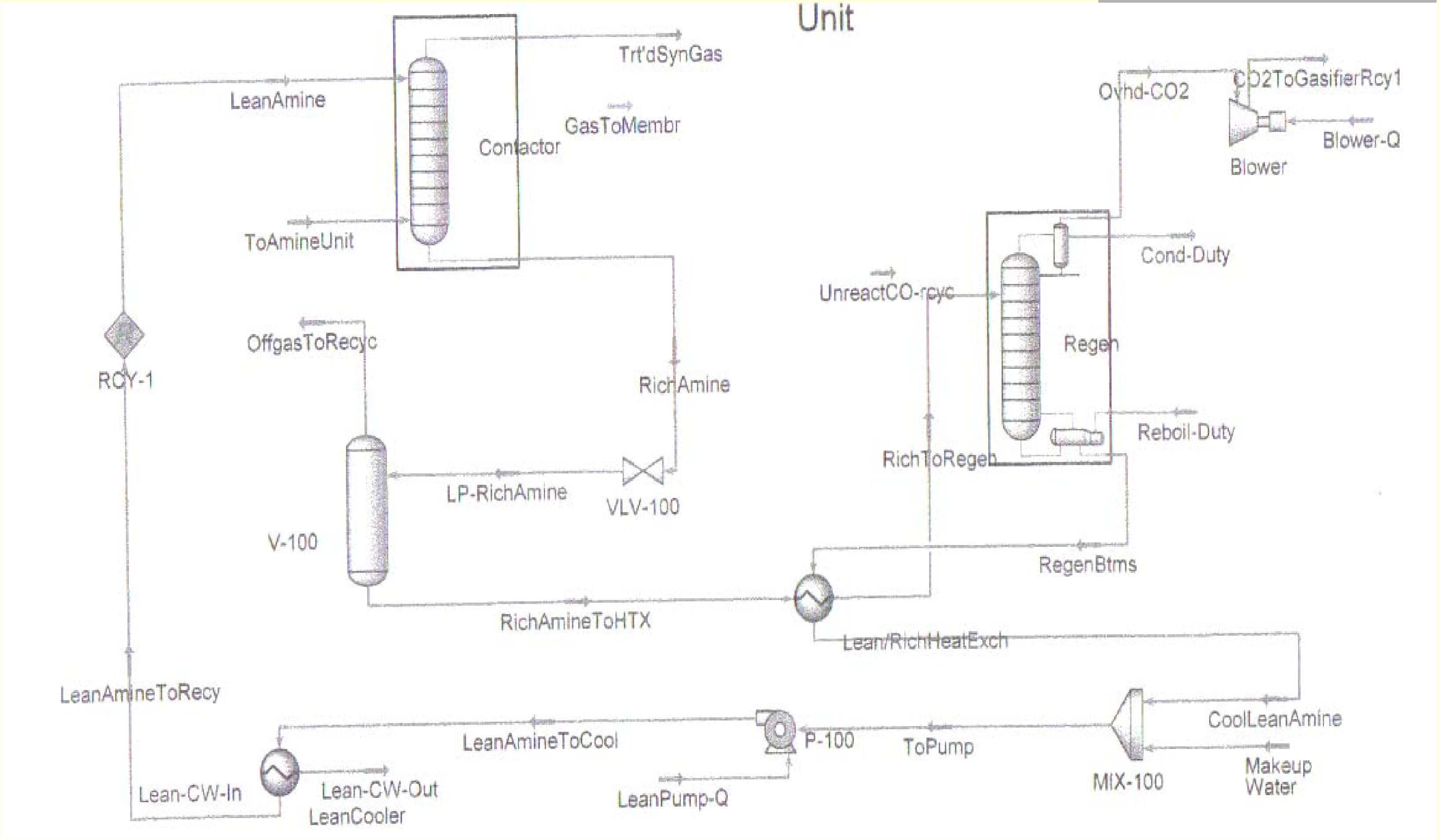
$$nCO + 2nH_2 \qquad CnH_2n + 10H + (n-1)\ H_2O$$

There are other reactions and competing reactions within the reactor depending upon other reactants and potential catalysts. Catalysts and conditions that allow the selective formation of alcohols while minimizing the formation of higher form of hydrocarbons is the thrust of our process.

Compression



Amine Unit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LeanAmine
GasToMembr
Contactor
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Ovhd-CO2
Blower-Q
Blower
Cond-Duty
UnreactCO-rcyc
Regen
OffgasToRecyc
RCY-1
RichAmine
Reboil-Duty
RichToRegen
LP-RichAmine
VLV-100
V-100
RegenBtms
RichAmineToHTX
Lean/RichHeatExch
LeanAmineToRecy
CoolLeanAmine
P-100
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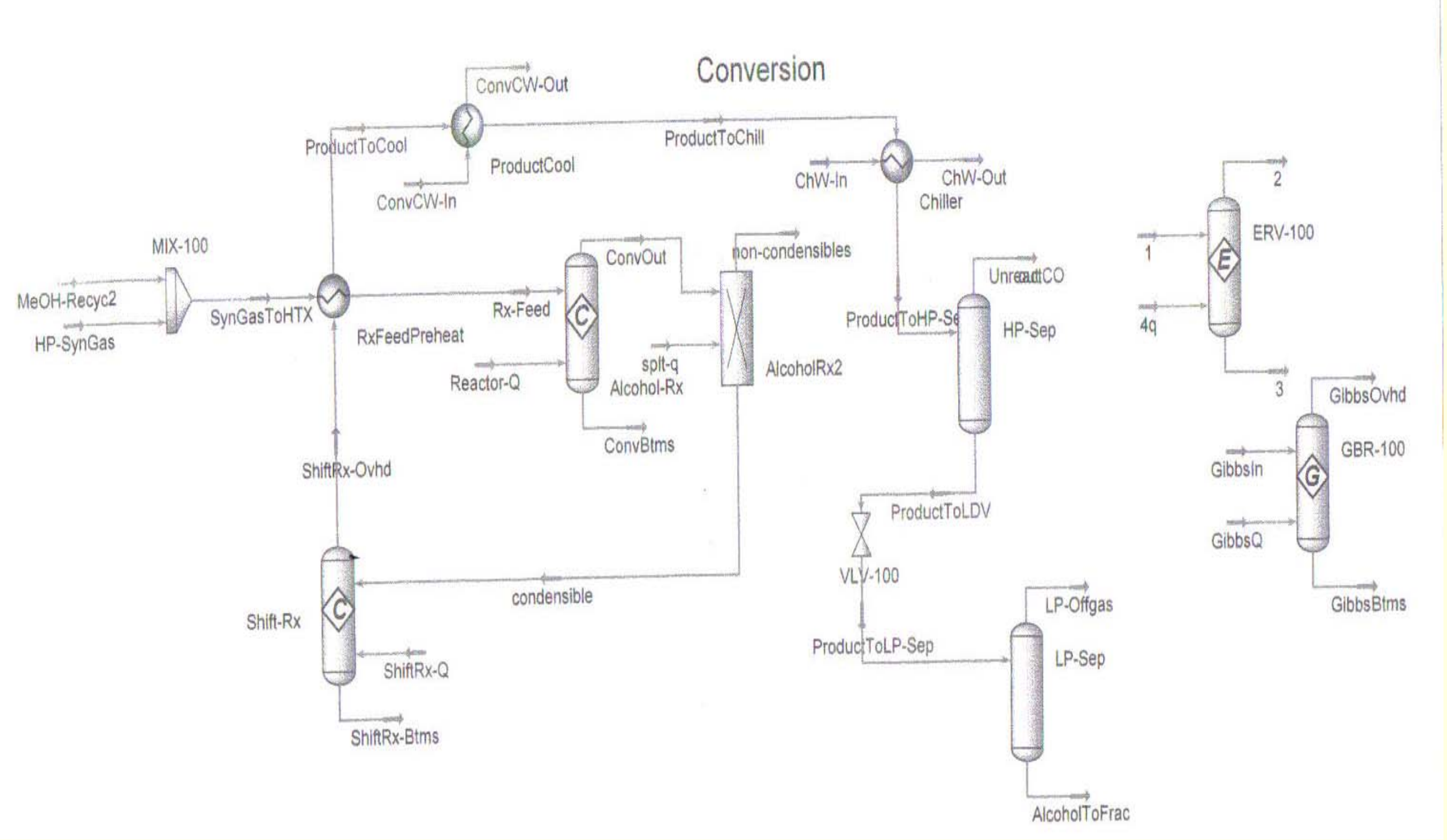
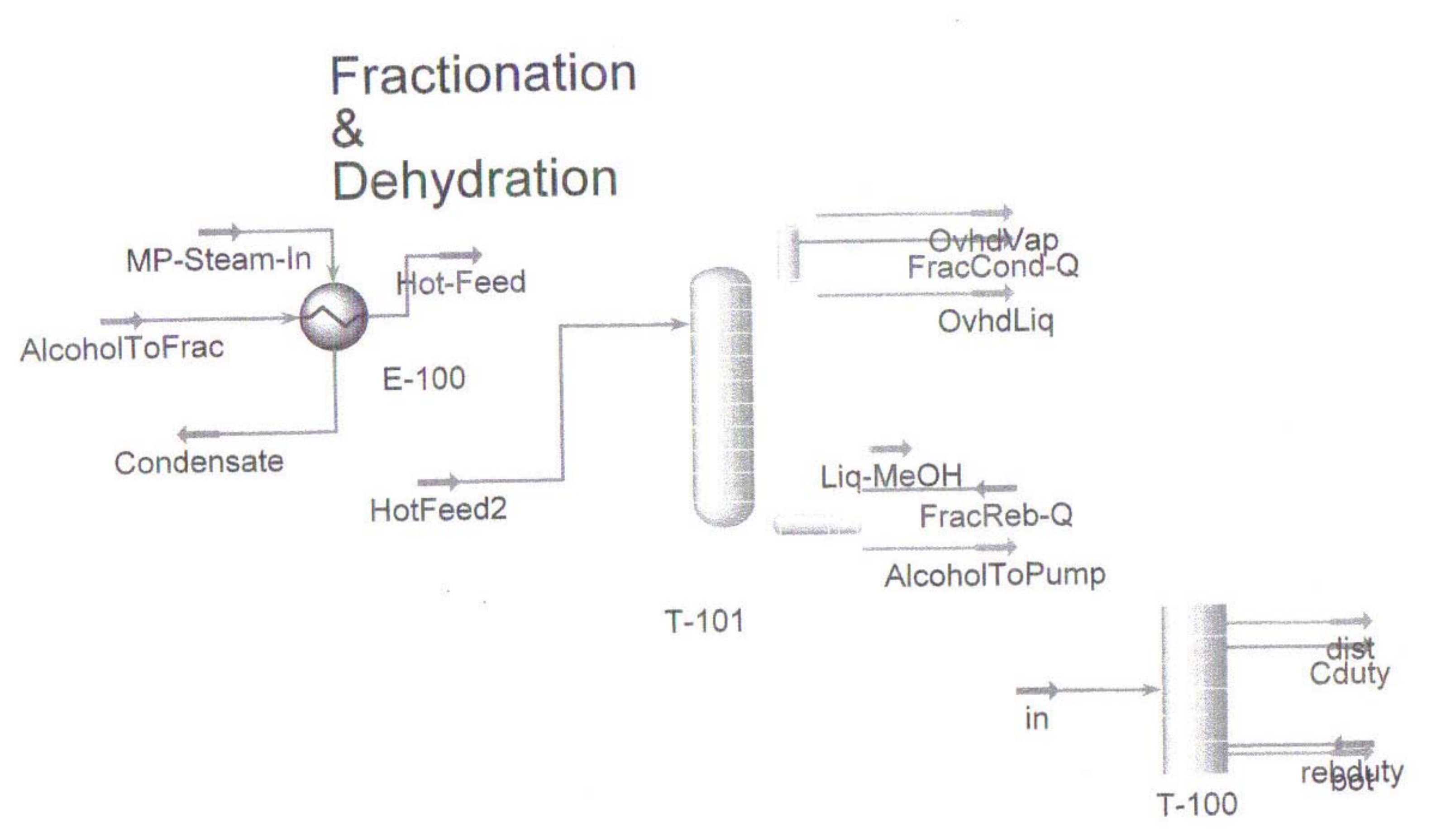
ToPump
Makeup Water
MIX-100
Lean-CW-In
Lean-CW-Out
LeanCooler
LeanPump-Q

Conversion


Conversion
ConvCW-Out
ProductToCool
ProductCool
ConvCW-In
ProductToChill
ChW-In
ChW-Out
Chiller
2
ERV-100
E
1
4q
3
MIX-100
MeOH-Recyc2
HP-SynGas
SynGasToHTX
RxFeedPreheat
Rx-Feed
C
Reactor-Q
ConvOut
non-condensibles
splt-q
Alcohol-Rx
AlcoholRx2
ConvBtms
UnreactCO
ProductToHP-Sep
HP-Sep
GibbsOvhd
GBR-100
G
GibbsIn
GibbsQ
GibbsBtms
ShiftRx-Ovhd
ProductToLDV
VLV-100
C
Shift-Rx
condensible
ShiftRx-Q
ShiftRx-Btms
LP-Offgas
LP-Sep
ProductToLP-Sep
AlcoholToFrac

Fractionation & Dehydration



BioConversion Technolgy Gasifier

Alcohol Plant