PRODUCTION OF REDUCING GASES FROM PETROLEUM PRODUCTS BY THE SHELL GASIFICATION PROCESS(*)

L.W. ter Haar,
Bataafse Internationale
Petroleum Maatschappij N.V.,
The Hague, Holland.

The development of processes for the direct reduction of iron ore with gaseous agents has been stimulated by two main factors, viz. the increasing demand for steel all over the world and the local shortage of suitable coal for the manufacture of metallurgical coke. The economic necessity to switch from coal to another source of carbon monoxide and hydrogen has also been felt in other than metallurgical industries. The rapidly increasing demand for water gas as basic material for processes such as the production of town gas, the synthesis of methanol and ammonia, the hydrogenation and hydrodesulphurization of petroleum fractions, and the hydrogenation of vegetable oils has resulted in an increasingly important call upon oil as a raw material in the production of gas for use in industry.

The Bataafse Internationale Petroleum Maatschappij, a service company of the Royal Dutch/Shell Group, decided in 1954 to embark on the development of an oil gasification process. The production of water gas complying with specifications of the chemical industry and of the town gas industry was the first aim of this development. At present four units, with oil throughputs varying from 50 to 200 tons per day, are in operation in Europe for the production of synthesis gas, and four other units, of which one for the production of a town gas component, are under construction.

It was recognized by Shell that specifications of gases for reduction purposes often will differ from those of water gas for industrial applications mentioned above. Special versions of the Shell process have therefore been developed for the manufacture of reducing gas of widely varying quality, composition and cost. Designs for pilot plant gasification installations suited for metallurgical research and development are available. In any version of the Shell process any gaseous or liquid hydrocarbon may be processed. Industrial size units of proven design await their use in the metallurgical industry.

In this paper both the production of high quality reducing gas by gasification of oil with oxygen and the production of gas of lower quality and cost by gasification of oil with air will be dealt with.

THE SHELL GASIFICATION PROCESS:

A. Description of the Process:

The Shell Gasification Process is based on the partial oxidation of a hydrocarbon feedstock either by oxygen, air enriched with oxygen or air. The reaction is a continuous non-catalytic flame type which takes place in a reactor specially developed for this purpose. When using oxygen or air enriched with oxygen, the partial oxidation has to be carried out in the presence of steam which is acting as a moderator. Instead of steam, carbon dioxide can be used if a CO-rich gas mixture is wanted. In the case of gasification with air no addition of steam to the reactor feed is required. The reaction conditions can be readily adapted to the feedstock selected. The process is capable of converting any gaseous and liquid hydrocarbon feedstock, from methane to residual oil.

This is significant advantage, since it permits adaptation to the most economic feedstock, which in different areas and under various market conditions with regard to the oil industry, does not necessarily have to be fuel oil, but may be for instance a low octane gasoline fraction.
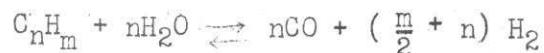
The term "partial oxidation" describes the net effect of a number of component reactions which occur in the flame. As is well known, such flame reactions are of a complex nature and not yet completely understood, but a good idea of their overall effect can be obtained by regarding them as essentially involving a two-stage mechanism.

As the first state, a complete oxidation reaction is assumed in which part of the hydrocarbon charged (or lighter ones derived from these by cracking reactions) is burned.

The oxidation reaction can be expressed as:

$$C_nH_m + \left(\frac{m}{4} + n\right) O_2 \longrightarrow nCO_2 + \left(\frac{m}{2}\right) H_2O$$

These reactions are highly exothermic and proceed rapidly to an equilibrium in which the oxygen is very nearly exhausted. The heat liberated is sufficient to raise a mixture containing a large stoichiometric excess of hydrocabons to the process temperature (1200 to 1500°C) and, at this temperature, to supply the heat requirements of subsequent and parallel endothermic reactions. These secondary reactions, which require the above high temperatures to attain reasonable reaction velocities, are of the types:

$$C_nH_m + nH_2O \rightleftharpoons nCO + \left(\frac{m}{2} + n\right) H_2$$

$$C_nH_m + nCO_2 \rightleftharpoons 2nCO + \left(\frac{m}{2}\right) H_2$$

It is thus seen that the primary combustion products serve as oxygen carriers, the oxygen of which is transferred to, and serves to gasify, the carbon contained in the unburned part of the hydrocarbons. These hydrocarbons need not be of any virgin type but may rather originate from thermal destruction, which occurs wherever the original charge is exposed to high temperature and is not yet in contact with oxygen or oxidizing gases.

Although hydrocarbons thus formed as short-lived intermediary products may facilitate the gasification reaction, they do not appear in the ultimate gas product to any appreciable extent. Whereas methane normally occurs in concentrations in the final gas of a few tenths of a volume per cent, hydrocarbons with a greater number of carbon atoms, which can be detected only in trace quantities, quickly die out as the size of the molecule increases. Intimate contact between the reactants ensures the simultaneous occurrence of the component reactions and thus prevents excessive temperatures which would result at any points where the primary reaction might locally attain dominance. A burner of special design is essential in order to obtain intensive mixing and thus uniform temperature distribution.

The distribution of the elements carbon, hydrogen and oxygen among the components of the wet gas ultimately produced is determined by the equilibrium of the CO shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
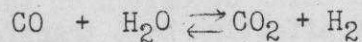
This equilibrium is, in fact, closely approached.

Residual quantities of two of the intermediary products formed by thermal destruction of the virgin hydrocarbon fractions, viz. of methane and carbon, appear in the effluent gas of the gasification reactor. This occurs in spite of the fact that their equilibrium concentrations under the prevailing chemical conditions are negligible or even zero: carbon should be consumed completely by either the Boudouard reaction

$$C + CO_2 \rightleftarrows 2\ CO$$
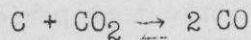
or the water gas reaction

$$C + H_2O \rightleftarrows CO + H_2$$
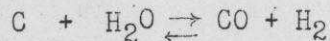
while methane should be similarly exhausted by the steam reforming reaction

$$CH_4 + H_2O \rightleftarrows CO + 3\ H_2$$
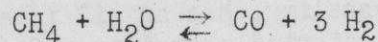
The experimental fact that these two products, although present in only small quantities, have not virtually disappeared is due to the relatively slow rate at which the consuming reactions proceed. It is then clear that an increase in process-temperature will entail a decrease of both

the relative amount of carbon found in the effluent gas and the concentration
of residual methane in it. The latter variable is so marked a function
of the reaction temperature that, for a given set of conditions, it can
be used as a fairly good indication of process temperature.

As already mentioned, the reaction temperature may vary
between 1200 and 1500°C. The pressure in the reaction space may range
from 3 to 40 kg/cm² abs and even higher, if required.

When air is used, the economic pressure range lies between
1 and 7 kg/cm² abs.

In view of the temperature at which the process takes place,
the utilization of waste heat is an economic necessity whenever the
product is required at a lower temperature. Despite the presence of
carbon in the gas, it has been possible to develop a highly efficient,
Shell-patented waste heat boiler which can produce steam of any
desired pressure in continuous operation. The overall thermal efficiency
of the process is thereby increased to a value of 87.5% for gasification
of 3000 seconds fuel with oxygen, for example.

The problems connected with the production, separation and
recovery of the small percentage of carbon which is formed were
successfully solved as the process was developed. The special construction
of the waste heat boiler prevents the carbon carried by the hot gases
from the combustion chamber from being deposited on the heat transmitting
surface, and thus from adversely affecting heat transfer. Downstream of
the waste heat boiler the carbon is separated from the gas streams by
means of water, a special process being used. The gases leave the
separation stage essentially free from carbon. The carbon-water slurry
is processed in special equipment to remove the water and to recover the
carbon in a form suitable for either further use or burning. Water
leaving the carbon recovery equipment is essentially free from carbon.

B. Pilot Plants and Commercial Installations:

The process was developed with the aid of two pilot plants
which had oil throughputs of 2 and 10 metric tons per day. It proved
possible to construct practically the entire plant from mild steel.
Experience both on pilot plants and commercial installations has shown
how commercial grade firebricks may be used for the brickwork of the
reactor.

Three plants of larger size have been built. One is
situated at the Shell Haven Refinery, England, and processes 200 tons
of oil per day. Another, constructed for the Union Rheinische
Braunkohlen Kraftstoffwerke, Wesseling, has an oil intake capacity
of 100 t/d, while a third plant started operating a few months
ago. All plants are composed of sets of reactors with an oil input
of 50 tons per day and their auxiliary equipment. In addition four
Shell Gasification Plants are under construction, including a 4-reactor
plant for the South Eastern Gas Board in England.

Standard reactors with capacities of 25, 50 and 100 tons per day of hydrocarbon input are available.

C. Production of Reducing Gases by Shell Process:

1. Gasification with oxygen and steam

<u>Manufacture of a water gas:</u>

Results typical of gasification of heavy fuel oil with oxygen in a commercial size reactor are given below:

Input :	Fuel oil, 3000 sec Redwood 1 viscosity:		1 kg
	Oxygen, as 100% but of 95% purity :		0.75 Nm3
	Steam to reactor	:	0.4 kg
Output:	Water gas, dry basis	:	2.95 Nm3
	Carbon	:	0.03 kg
	Steam from waste heat boiler	:	2.3 kg

The dry gas has approximately the following volumetric composition:

Hydrogen	46.1%
Carbon monoxide	46.9%
Carbon dioxide	4.3%
Total hydrogen sulphide and carbonyl sulphide	0.9%
Methane	0.4%
Total nitrogen and traces of other gases	1.4%
Carbon content	less than 1 mg/Nm3

The gas is a very suitable starting material for the synthesis of chemicals such as ammonia and methanol, and can also be used as a blending component for town gas manufacture.

Water gas has strong reducing properties and may be used as such in the direct reduction of iron oxides. A direct reduction process which may be mentioned in this connection is, for instance, the Kellogg (Hyl) process.

Manufacture of hydrogen from water gas:

Hydrogen can be produced from a crude gasification product by applying conventional catalytic carbon monoxide conversion with steam followed by removal of the carbon dioxide formed. According to the literature *) the H-iron process requires hydrogen at elevated pressure (250 psig is mentioned). Obviously a pressure gasification process has a number of advantages for this application, the more so since the treating and conversion of the gas is also preferably carried out under pressure. The Shell Gasification Process, whose pressure can be adjusted to suit the operating conditions of the further plant, is therefore considered an excellent tool for this purpose.

Manufacture of a CO-rich gas:

For some metallurgical processes a gas rich in carbon monoxide is required. Such a gas can be produced by gasification with oxygen in the presence of sufficient carbon dioxide and steam. A gas with, for instance, a carbon monoxide to hydrogen ratio of 2 can be produced under the following conditions:

Input :	Fuel oil, 3000 sec Redwood I viscosity:		1 kg
	Oxygen, as 100% but of 95% purity	:	0.80 Nm3
	Carbon dioxide to reactor	:	0.52 kg
Output:	Dry gas	:	2.99 Nm3
	Carbon	:	0.03 kg
	Steam from waste heat boiler	:	2.5 kg

The dry gas has the following analysis, in volume per cent:.

Hydrogen	29.3%
Carbon monoxide	59.2%
Carbon dioxide	8.8%
Methane	0.4%
Total hydrogen sulphide and carbonyl sulphide	0.8%
Nitrogen and argon	1.5%

2. Gasification with air:

If, as part of a beneficiation process, hematitic ores have to be partially reduced to an artificial magnetite, this is preferably effected with a gas having weak reducing properties. A direct route to

---

*) A.M. Squires and C.A. Johnson, The H-Iron Process, Journal of Metals, April, 1957, p. 586.

the manufacture of such a gas is given by gasification with air rather
than with oxygen. The pressure range in which gasification with air is
more economical than that with oxygen lies between 1 and 7 kg/cm^2 abs, as
already stated. Operating data typical of gasification of Bunker C fuel
oil with air are given below:

Gasification pressure, psig	15	50
Air preheat temperature, oC	550	550
Gas composition at 20oC, percent volume basis		
Carbon monoxide	23.6	21.6
Hydrogen	16.5	13.3
methane	0.1	0.1
carbon dioxide	1.5	2.6
nitrogen	56.5	61.3
hydrogen sulphide and carbonyl sulphide	0.4	0.4
water vapour	1.5	0.7
Lower calorific value, kcal/Nm3	1150	1010
Carbon content, ppm	100-300	10-30
Gas yield on feed, Nm3/kg	6.15	6.45
Steam produced on feed, kg/kg	3.6	4.65

The low carbon content of the gas is obtained by removing the
carbon in the same type of equipment as used for gasification with oxygen.
For many applications, however, carbon removal might not be necessary.
Without carbon removal the carbon content of the gas will be of the order
of 2500 ppm.

Gasification of liquid fuels with air might also find application
in the production of gaseous fuel for kiln processes, which require accurate
control of reaction temperatures throughout the kiln (the R-N process for
example).

For direct reduction to sponge iron, gases with a very low
water vapour and carbon dioxide content are required. In the sponge iron
production process less use of heat exchange can apparently be made than
in magnetic roasting, so that the content of inert materials, like
nitrogen, in the gas should be reduced as much as possible. A pressure
gasification process using oxygen has the advantages of easy removal
of water vapour and of carbon dioxide from the gas, and further that
there is a low content of inert material. Nevertheless, gasification
with air should be given serious consideration for production of
reducing gases for total reduction because of its lower manufacturing
cost, as will be shown in the following paragraph.

D. Cost of Reducing Gas from Oil:

For the cost of reducing gas no absolute figures can be given
in this paper because the cost of oil, labour and maintenance and the rate
of depreciation will largely depend on local conditions, which will differ
from case to case. However, a general indication of the cost of reducing
gas is obtained already by expressing it in terms of the cost of oil, as

shown in the table below. The costs shown for water gas and hydrogen include the cost of oxygen required for gasification. The range in gas cost shown originates from variations in cost of oil and in the rate of depreciation.

Production cost of reducing gas from oil *)

Reference: Oil price per unit of lower heating value (l.h.v.): 1

Type of gas	Cost of gas per unit l.h.v.
Low calorific value gas,	
1150 kcal/Nm3, 100-300 ppm carbon	1.4-1.6
1000 kcal/Nm3, 10-30 ppm carbon	1.5-1.8
Water gas (93% vol of CO+ H_2),carbon-free	2.4-3.0
Hydrogen of technical grade	3.4-4.7

*) Note: Gasification capacity about 200 tons daily throughput of oil.

It is concluded from the above comparison that, for equal cost of reducing gas per unit of iron, the overall thermal efficiency of a reduction process using low calorific gas can be allowed to be only 55-60% of that of a reduction process on water gas for example.

E. Gasification Feedstocks:

It should be stressed that the Shell Gasification Process is capable of handling a wide variety of hydrocarbon feedstocks, ranging from natural gas to C-grade fuel. The Shell process gasification efficiency is equally good for both light and heavy feedstocks. The choice of the feedstock will therefore be governed by factors other than the technology of the Shell Gasification Process, such as the availability and price of the feedstock.

F. Conclusions:

A number of examples have illustrated the versatility of the Shell Gasification Process for the production of a wide variety of hydrogen and carbon monoxide mixtures from any oil fraction. Oxygen, air enriched with oxygen and air can be used as oxidant in this process.

For the production of gas to be used under pressure oxygen has great advantages, since it offers economic gasification under pressure and easy removal of unwanted by-products like water vapour and carbon dioxide.

In the production of reducing gases at low pressures, on the other hand, air has great economic advantages over oxygen. Reducing gases produced from oil fractions by gasification with air will no doubt find application in the processing of low grade hematitic iron ores. Whether this low cost gas, characterized by a high content of inert material, can also be economically used in direct reduction to sponge iron will depend, among other things, on the extent to which use can be made of heat exchange in sponge iron production.

For the manufacture of reducing gas with both oxygen and air Shell have available proven designs of reactors ranging in capacity from 2 to 100 tons per day of oil throughput. This range covers the requirements of both pilot plants and commercial plants in the metallurgical industry.

- - - -

/SKB.