DEVELOPMENT OF A TECHNICAL PROCEDURE FOR THE PRODUCTION OF ACETYLENE FROM RESIDUAL OILS AND COAL BY THE ELECTRIC ARC PROCESS

Dr. R. Müller, Dr. C. Peuckert
Chemische Werke Hüls Aktiengesellschaft, Marl, Germany

ABSTRACT

In an 80-kw pilot plant, heavy oils have been cracked to form acetylene and ethylene in an H_2 plasma jet, and, in doing so, on-stream periods of several hours could be achieved. For this purpose, specific measures had to be taken to avoid caking upon the walls and to improve the mixing of oil and plasma jet, these difficulties becoming even more problematical in the case of coal being employed. Up to now, an energy consumption of 15 kwh/kg C_2H_2 has been reached for the yields obtained by this procedure, which still seems to be improvable.

1. INTRODUCTION

The electric arc process of Chemische Werke Hüls employed for the production of acetylene from hydrocarbons is the only electric arc process in the chemical industry being used for even more than forty years. The present capacity is of the range of 120,000 t C_2H_2/a at an annual energy consumption of 1.5 million Mwh. Since start-up, this process has constantly undergone further development to enlarge its field of application (Tab. 1).

At all stages of development, a gas whirl-stabilized high-voltage arc has been employed; in case of hydrogen being used, modifications (1) had to be made to the combustion chamber geometry considering the specific flow conditions. It may be seen from the table that in those cases where the electric arc process has been tested on a commercial scale, only gaseous or liquid hydrocarbons with a comparatively high content of low-boiling components have been used. With increasing crude oil shortage, however, the utilization of the high-boiling components of crude oil and the use of coal have become more and more interesting. This is why, already in the early seventies, trial runs were carried out by Chemische Werke Hüls in a pilot plant to test the pyrolysis of crude oil residues in an H_2 plasma. From the end of 1980, also the pyrolysis of coal has been tested in this plant with a view to developing a technically usable process. Bergbauforschung GmbH, Essen, equally takes part in this development by carrying on their laboratory tests.

2. EXPERIMENTAL SETUP

The plant consists of a plasma generator with a high-voltage arc of up to 80 kw. Stabilization of the arc is effected by tangential feed of hydrogen into the whirl chamber. With regard to the hydrogen jet entering the reactor through the anode nozzle, various energy densities of between 2.8 and 3.8 kwh/Nm^3 can be employed. With falling pressure, power input slightly decreases (Fig. 2). Thermal loss in the plasma generator is of the range of about 3 %.

Directly behind the anode nozzle, the plasma jet is mixed with the oil and is converted. After a residence time of a few milliseconds, the oil/gas mixture is quenched by injecting hot oil through nozzles, and the bulk of the carbon black is washed out. This kind of quenching procedure is of advantage, as it enables the recovery of the cracked gas enthalpy in the form of steam. Then the unconverted oil components are further condensed and are recycled to the reactor after mixing with fresh oil.

In the case of coal being employed, the plasma generator remains unchanged. Modifications are made solely with regard to reaction and recovery (Fig. 3). Here, the dried coal (Tab. 2) is metered from two storage containers through two proportioning screws into a hydrogen stream and is then injected into the reactor through nozzles. Coal proportioning is effected by screw speed adjustments. After leaving the reactor, the reaction gases are water-quenched by means of nozzles, the carbon black and coke formed are separated in a solids separator, and then the gases are further cooled and purified by water and oil scrubbing. A vacuum of about 0.5 bar can be achieved by means of a water ring pump.

The amounts of gas can be measured through orifice plates. Samples can be taken either immediately following the quench or after gas purification.

3. PYROLYSIS OF CRUDE OIL RESIDUES

It is generally known that, in the pyrolysis of hydrocarbons, deposits of carbon black- and coke-type components easily form on the walls, thus impeding a continuous operation. This is why, in considering as to whether a process is suitable for production, not only optimum yields and minimum energy consumption should be decisive, but the process should be designed such as to enable a continuous operation of the plant over a prolonged period at the highest possible yields, i.e. the following objectives are to be achieved:

- both intense mixing of plasma jet and oil to maximize acetylene yields and

- prevention of carbon deposits on the reactor walls to maximize on-stream periods

For this purpose, various types of reactor have been developed with differently designed plasma jet/oil mixing zones and different methods of feeding the oil into the reactor (e.g. tangentially or radially). Furthermore, the above objectives were found to be achievable only within a comparatively narrow range of reactor diameters, as in case the reactor diameter is too small, choking readily develops from the mixing zone, and in case the reactor diameter is too large, insufficient mixing entails low acetylene yields. Also, the yields achieved by a specific design are highly dependent on the characteristics of the oil used. As the chemical characterization of these high-boiling oils is practically impossible, the effects of their chemical structure cannot be dealt with, while it is easier to determine the effects of their boiling range. For this purpose, mixtures of various crude oils and heavy residual oils have been prepared.

Typical yields achieved by the pyrolysis may be taken from Fig. 4, where acetylene and ethylene yields per unit of power are shown, both decreasing with lessening content of low-boiling components. Analogously, the amount of H_2 obtained decreases, while, at the same time, the amount of carbon black increases. This suggests that, with decreasing content of low-boiling components in the oil, it becomes more and more difficult to reduce excess temperatures in the middle of the plasma jet, these temperatures being the very reason for the formation of carbon black.

The tests have shown that, by an electric arc process, even heavy residues can be cracked to form acetylene and ethylene in an electric arc plasma, yielding results which from the technical point of view are absolutely satisfactory.

4. PYROLYSIS OF COAL

The above-mentioned connection between mixing and caking upon the walls becomes even more problematical when coal is employed, as, when heated, coal becomes plastic within a certain range of temperatures where it has a particularly strong tendency to caking. This is why, in the beginning, only on-stream periods of a few minutes were achieved, with the reactor being designed in the same way as for operation with oil, and no steady values were obtained. Also variations in coal feed - e.g. velocity, radial or tangential feed - or the use of different materials, as Cu, graphite or sintered metal, did not result in appreciably prolonged on-stream periods. Pertinent tests, however, are still under way. As a first measure to obtain sufficient on-stream periods, washing cycles with water or water vapour were initiated in order to split off or gasify the cakes. After various designs had been tested, reproducible on-stream periods of about 1 hour could be achieved at short washing cycles. During washing, nearly no acetylene is produced. The reproducibility of the tests may be taken from Tab. 3. The values shown relate to the pyrolysis phase during the washing cycles. Energy consumption for several cycles including the washing phase is about 10 % higher.

Energy consumption is still clearly higher than for heavy oil cracking. This is due to the insufficient mixing of coal and plasma jet. Flow tests in glass reactors have shown that the coal flows in strands predominantly along the reactor walls. A comparison of the coal and coke analyses (Tab. 1) equally shows that the volatile content of coke is still comparatively high, the mean grain diameter, however, having clearly decreased. The mean gas outlet temperatures are of the range of 2,000 °C; in calculating these temperatures, loss and conversion have been taken into account; also the values thus obtained are indicative of a less intense mixing. A more intense mixing can be achieved for example by a decrease in reactor diameter, as may be seen from the following values (Tab. 4).

In addition to varying diameters, a great many other reactor designs have been developed to improve the mixing of coal and plasma jet; in these developments, attempts have been made to reduce the whirl effect by flow separation, orifice restriction or baffles. Such designs having been developed for glass reactors, they did not stand the test in practice (see Fig. 5), as they do not meet the high thermal requirements set by the plasma jet. In addition to these geometrical parameters, the effects of pressure and of the energy density of the plasma jet have been investigated, and both parameters proved to have little effect on the cracking efficiency. Further improvements, however, could be made in the course of the tests, i.e. the best value achieved up to now is an energy consumption of about 15 kwh/kg C_2H_2 at a gas yield of 35 %.

Considering, at the above-mentioned yields and gas outlet temperatures, the supply of electrical energy to the plasma reactor with regard to its distribution among the individual steps, it may be seen from Fig. 6 that only 20 % of energy is converted to chemical energy. Besides the cooling water loss in generator and reactor, the major part of energy remains in the plasma gas and cracked gas enthalpy, and, with the conventional quenching procedure being employed, this energy portion gets lost through the quench water. To ensure a high process efficiency, the largest possible amount of this energy has to be recovered.

The most important objective to be achieved doubtlessly is a further increase in chemically bound energy, but even if this is reached, about 60 % of energy still remains in the gas as enthalpy portion, according to optimistic estimates made by us. In our commercial process for cracking gaseous hydrocarbons, part of this energy is used for the production of ethylene by injecting volatile hydrocarbons through nozzles. Similar measures are planned to be taken also in this case. Even then, however, 50 % of energy remains in the gas at off-gas temperatures of about 1,000 °C.

In a technically efficient manner, this portion of the electric energy can be recovered only in the form of steam. Major technical difficulties, however, still have to be overcome in connection therewith, as may be seen from the comparison shown below:

Operating principle	Disadvantage
Indirect gas cooling by heat exchangers	low quenching speed results in loss of acetylene; high abrasion in the heat exchangers by high solids content
Water quench	no energy recovery
Gas quench	large amount of recycle gas entails an increase in energy requirements by gas recycling as well as an increase in investment
Oil quench	high oil consumption for discharge of the carbon black/coke mixture

Only practical testing of the quenching procedures shown above, which already has been taken up, will prove which of them ensures both optimum heat recovery and good technical practicability.

Though a large portion of the enthalpy content of the gases can be recovered by a suitable quenching system, whereby the process efficiency can be clearly improved, it still remains a fundamental disadvantage of plasma processes that, by these quenching procedures, electric energy is converted to steam.

We wish to express our thanks to the Land of North Rhine-Westphalia for sponsoring the developmental work for the pyrolysis of coal.

Literature:

(1) R. Müller, Methodicum Chimicum, Vol. 4, Stuttgart, New York, 1980

TABLE 1

The electric arc processes of Chemische Werke Hüls - stages of development				
Operating principle	Plasma gas	Feedstock	Stage of development	Electric power
single-step	gaseous hydrocarbons	gaseous hydrocarbons	production plant 120.000 t C_2H_2/a since 1939	8.5 Mw
tow-step	hydrogen	liquid hydrocarbons like LNG, crude oil	prototype plant 1970/72	8.5 Mw
two-step	hydrogen	liquid hydrocarbons up to heavy residual oils	pilot plant 1972	80 kw
two-step	hydrogen	coal	pilot plant 1980 (1981)	80 kw (500 kw)

TABLE 2

Analysis of coal and coke				
Type		Feed coal Westerholt	Coal (waf)	Coke (waf)
Volatiles	%	38.4	42.8	15.70
Ash	%	6.9	-	-
Water	%	3.4	-	-
C	%	75.40	84.06	92.87
H	%	5.22	5.82	5.79
O	%	6.99	7.70	-
N	%	0.53	0.59	0.31
S	%	1.56	1.74	1.22
d_{50}	(μ)	60	-	23

TABLE 3

Reproducibility of tests					
Plasma gas (Nm^3/h)	25.0	25.0	25.5	24.3	22.2
Electric arc power (kw)	76.3	72.8	72.5	78.0	73.2
Energy density plasma gas (kwh/Nm^3)	3.05	2.91	2.84	3.21	3.30
Coal feed (kg/h)	14 ± 10 %				
Acetylene concentration (vol. %)	8.4	9.2	8.8	9.3	9.1
SER (kwh/kg C_2H_2)	18.2	16.2	17.3	17.3	17.0
Gas yield (%)	33.6	36.6	34.7	34.4	34.7
Acetylene yield (%)	25.9	28.1	25.7	27.9	26.4

TABLE 4

Effect of the reactor diameter on energy consumption and yield			
Rel. reactor diameter	0.7	1.0	1.3
SER (kwh/kg C_2H_2)	18.7	26.5	43.8
Gas yield (%)	37.4	33.8	7.5

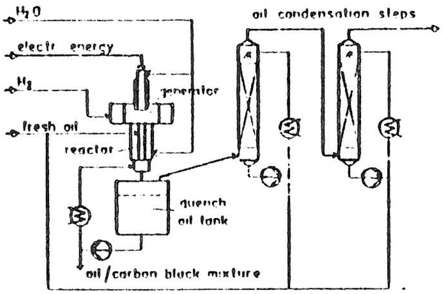


Fig. 1 Design of pilot plant for the pyrolysis of oil in an H_2 plasma

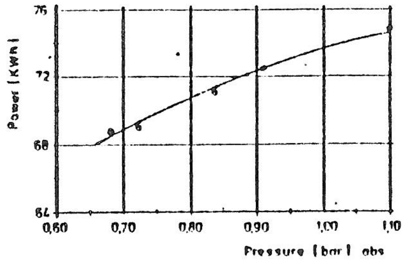


Fig. 2 Power input as a funktion of pressure

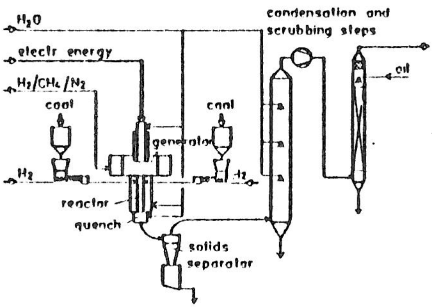


Fig. 3 Design of pilot plant for the pyrolysis of coal in an H_2 plasma

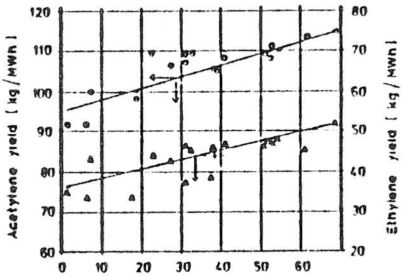


Fig. 4 Acetylene and ethylene yields as a funktion of the light-boiling components

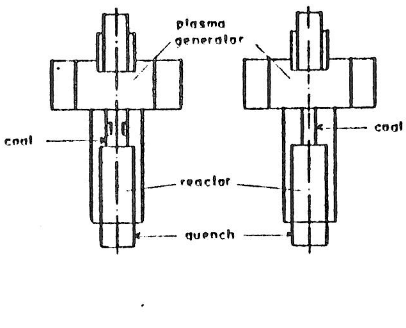
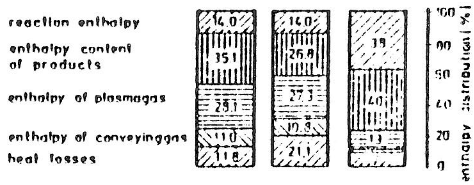


Fig. 5 Basic setup of different reactors for the pyrolysis of coal



energy density of plasmagas [kWh/Nm³]	2.50	3.05	4.00
calculated temperature [°C]	2000	2007	1700
coal feed [kg/kWh]	0.24	0.20	0.28
conveying gas [Nm³/kg]	2.6	2.2	0.6
comments	own measurement		target value

Fig 6 Energy distribution