53-0160

May, 1960 Translation .175

MINISTRY OF POWER
CHIEF SCIENTIST'S DIVISION

Obtaining Gases of a Given Composition When Gasifying Solid Fuels Under High Pressure

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Khim. Tekhnol. Topliv i Masel, July, 1958. 3. (7). 1-8.

In modern chemical industry the manufacture of synthesis gases by gasifying solid fuels has become general. However, no attempt has been made to link up the gasification processes with the subsequent synthesis which often leads to unfavourable economic results. Thus, for instance, the predominant industrial gas synthesis processes are carried out at high pressure, whereas gasification of fuel with synthesis gas production, has been conducted at approximately atmospheric pressure.

With pressure gasification, a compressed gas is obtained with minimum power consumption, ready for chemical synthesis and for long-distance transmission. When operating pressure gasification, the dimensions of the equipment and transmission lines can be considerably reduced, thus ensuring the compactness of the plant.

Pressure gasification to-day is operated only as a method for manufacturing gas with increased C.V. mainly for use as town's gas. Scientific data establishing conditions of high pressure gasification needed for obtaining gases of a given composition (synthesis gas), are lacking.

Thermodynamic investigation of the gas producer process (1) has shown that by varying the process temperature and the blast composition it is possible to obtain with high pressure operation the required ratio of reactive components in the gas.

Gas, containing reactive components, required for the chemical synthesis of hydrocarbons (H_2:CO ratios between 1 and 3) is obtained by pressure gasification at comparatively low temperatures (up to 1000°); increased pressure speeds up the production of the required gas at higher temperatures.

In order to obtain high pressure gas suitable for NH_3 synthesis, higher temperature (1100-1200°), as well as oxygen-enriched air blast, is required.

Thermodynamic analysis of the process shows, however, that the use of high pressure in gasification of fuel results in an increase in the gas of components undesirable for the synthesis (CO_2, CH_4).

Our investigations were aimed at studying the high pressure gas producer process with a view to obtaining gases having the required ratio of reactive components but with a minimum methane-content.

Experiments were carried out under laboratory conditions; the diagram is shown in Fig. 1. The main piece of equipment was in the shape of a cylinder made of stainless steel 800 mm in height and having an internal diameter of 150 mm. Inside the cylinder a reaction tube was placed; this was made of stainless steel, and was 500 mm long with an internal diameter of 50 mm. An 11 kW electric preheater was fixed on the tube. In order to limit losses, heating of the outer wall of the vessel was effected by a separate electric heater. The reacting gases (O_2, CH_4, CO_2) were passed from the cylinders through a throttle valve and a high pressure flow meter to the pressure equaliser and entered the main vessel immediately above the reaction tube. The steam, superheated to a temperature of 350-400°, was fed into the lower part of the annular space between the wall of the instrument and the reaction tube; from there it passed into the fuel bed from above.

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~~1.80~~
~~1.80~~
#1.10

In order to achieve better mixing of the reacting gases and the steam, a 100 mm. high perforated cylinder was inserted and this was filled with 8-10 mm. fireclay.

The gaseous product was led off immediately below the reaction tube and after passing through an expansion valve was fed into the low pressure system. During the experiments the temperature of the reaction zone was recorded by platinum/platinum rhodium thermocouples, placed at the centre of the bed at a distance of 15 and 350 mm from the bottom of the reaction tube. The temperature of the blast was measured on entering the reaction vessel.

Determining the Conditions Limiting Methane Formation in High Pressure Gasification of Fuel

Previous investigations of the mechanism of gas production at high pressure (2) have shown that the causes of methane formation in pressure gasification of fuels are the thermal decomposition of the organic matter of the fuel and methane synthesis reactions, $CO + 3H_2$ and $C + 2H_2$.

When the low temperature carbonisation process is conducted under pressure a smaller methane yield may be obtained for a given fuel by reducing the pressure and by carrying out the process in a water vapour medium (3).

When studying methane formation by gas synthesis, the slight progress of these reactions in the oxygen zone where high temperatures prevail, must be stressed.

The principal formation of methane in pressure gasification takes place in the reduction zone.

In order to determine the conditions restricting methane formation in pressure gasification, we have carried out two series of experiments:-

1. Experiments on gasifying peat semi-coke with a steam/oxygen mixture ($H_2O:O_2$ = 1, 5 and 10) at pressures of 1, 20 and 50 atm.

2. Experiments in order to study the reactions between different mixtures of $CO_2 + H_2O$ ($CO_2: H_2O$ = 0.2, 1.0 and 2.0) with peat semi-coke at temperatures of 750-950° and pressures of 1 and 20 atm.

The blast rate in all experiments was similar, viz. 50 l/min., corresponding to a linear velocity of the blast of 0.425 m/sec. (under normal conditions). The initial height of the bed was 450 mm. The weight of the charge was approximately 300 g. The particle size of the peat semi-coke was 3-5 mm. An analysis of the peat semi-coke is given below:-

Moisture content ...	7.09	Carbon ...	89.31
Ash	14.42	H ...	2.35
V.M.	14.22	N ...	2.78
		S ...	0.42
		O ...	5.14

During the experiment, at given time intervals gas samples and temperatures in the fuel bed were taken.

Each gas sample taken at a given time, represented a different level of the bed. The gas obtained was, therefore, analysed, and the height of the bed was calculated each time from the amount of burnt out carbon.

The experiments confirmed the findings of thermodynamic investigations on the possibility of obtaining by pressure gasification a gas with a predetermined ratio of carbon monoxide and hydrogen. For each given ratio of $H_2:CO$, a particular, optimum blast composition is required as well as the appropriate pressure (Fig. 2).

All other conditions being equal, increased pressure results in an increased ratio of $H_2:CO$ in the gas. However, a more appreciable effect on the ratio of $H_2:CO$ is exerted by the composition of the blast. General experimental data on the rate of methane formation in the pressure gasification of peat semi-coke are shown in Fig. 3.

As shown in the diagram, the rate of methane formation increases with increased temperature in the bed and increased pressure. However, above 1300-1350° the rate falls, which apparently is explained by the acceleration of methane conversion with undecomposed steam.

The methane-content in the gas decreases considerably with a decrease in the height of the fuel bed.

During the second series of experiments methane formation in the reduction zone was examined.

Fig. 4 shows methane-content in the dry gas as a function of the temperature with different ratios of CO_2: H_2O and at pressures of 1 and 20 atm.

An increased ratio of CO_2: H_2O results in a decrease of the CH_4-content in the gas.

With increased pressure (all other conditions being equal), the methane-content of the gas is increased.

Temperature increase in the process results in increased methane-content in the gas; the increase is higher, the higher the pressure and the lower the ratio CO_2:H_2O. The seeming discrepancy of this result with the conclusions of thermodynamic analysis, in which a decrease in the methane-content was assumed to take place with increased temperature, may be explained by the fact that at the temperatures investigated equilibrium had not been sufficiently established.

In the gasification zone, the reactions proceed step-by-step (decomposition of steam, methane synthesis and methane conversion). The result is that the rate of the methane conversion reaction at the temperatures employed in the experiments, and the residence time of the gases in the fuel bed, are not adequate to establish a complete equilibrium.

At the present stage of development of pressure gasification in a gas producer, conditions have not been created that favour methane-conversion with steam and carbon dioxide, although these reactants are present in the steam/gas mixture within the process.

At the moment, when the presence of methane is first observed in the gas, the gas stream has already entered the low temperature zone, where methane conversion occurs only slightly.

The experiments have shown that the most effective method of restricting methane formation in pressure gasification is by controlling the composition of the gas mixture entering the reaction zone.

Determination of the Conditions Contributing to Methane Conversion in High Pressure Gasification of Solid Fuels

We have already indicated that in existing high pressure gasifiers methane conversion is slight, although the required reactants are present in the gas mixture. In order to utilize this reaction to obtain gases of a given composition it is necessary to study the conditions favouring the reaction in the fuel bed to be gasified, as well as in a separate apparatus employing an inert charge.

With this in view, we have carried out a thermodynamic and experimental investigation of the reaction between methane and steam at high and normal pressures in the presence of coal or an inert charge.

As is known, the reaction $CH_4 + H_2O$ is carried out industrially at atmospheric pressure in the presence of catalysts. This reaction, carried out in the presence of a solid fuel, however, hasn't been used industrially and has been hardly investigated.

A small number of experiments in this direction was carried out in 1930 by N. A. Klyukvin (4); the results, however, were not such as to permit any conclusions whatsoever with regard to this reaction and the effect of individual factors on its course.

At present no published material is available on the thermodynamic equilibrium of the reaction $CH_4 + H_2O$ at high pressure in the presence of coal or an inert charge.

Only theoretical figures are available for gas equilibrium composition; these were calculated by V. A. Karzhavin (5) from data obtained during methane conversion at normal pressure with various amounts of steam at temperatures of 500-1200° over coal and fireclay.

We have calculated the equilibrium of the reaction $CH_4 + H_2O$ at pressures 1, 20 and 40 atm, temperatures of 700-1100°C, and $H_2O:CH_4$ ratios of 1, 5 and 10, in the presence of carbon or an inert charge. The table shows the degree of methane conversion with steam obtained by these calculations.

Temperature °C	Reaction occurs	$H_2O:CH_4 = 1$			$H_2O:CH_4 = 5$			$H_2O:CH_4 = 10$		
		1 atm.	20 atm.	40 atm.	1 atm.	20 atm.	40 atm.	1 atm.	20 atm.	40 atm.
700	over coal	75.6	6.0	5.6	57.0	0.0	0.0	50.9	0.0	0.0
	without coal	76.2	27.8	20.8	99.5	67.9	54.2	100.0	89.0	76.6
900	over coal	76.0	54.5	43.6	93.0	23.5	0.0	88.7	0.0	0.0
	without coal	96.7	67.9	52.5	100.0	97.9	93.4	100.0	99.6	99.0
1000	over coal	96.0	70.2	56.5	96.9	46.1	17.5	94.0	12.2	0.0
	without coal	98.5	80.5	69.4	100.0	99.5	98.0	100.0	99.9	99.9
1100	over coal	99.0	83.0	72.0	98.0	69.6	47.5	97.0	48.0	15.5
	without coal	99.4	89.5	81.5	100.0	100.0	99.7	100.0	100.0	100.0

The calculation of the thermodynamic equilibrium of the $CH_4 + H_2O$ reaction, has shown that the optimum conditions for this process are:-

(a) with an inert charge - temperature above 900°; $H_2O:CH_4$ ratio ≥ 5; all pressure ranges examined;

(b) in the presence of coal - temperature above 1100°; $H_2O:CH_4$ ratio = 1 and below; at the lowest possible pressure.

Under these conditions practically complete methane conversion is obtained, both in the presence of coal and an inert charge.

In evaluating these optimum conditions with regard to the pressure gasification of solid fuels in practice, it must be noted that to carry out the reaction $CH_4 + H_2O$ in the presence of coal is hardly feasible.

The temperatures of pressure gasification of solid fuels with dry ash removal are always below optimum, since they are limited by the ash melting temperature, i.e. of the order of 1100°.

During the process large amounts of excess steam are produced and, therefore, the $H_2O:CH_4$ ratio in the unpurified gas considerably exceeds (for instance 6-10 times when working with brown coal) the value, which thermodynamically is the most advantageous for the conversion.

The $CH_4 + H_2O$ reaction in the presence of coal can only be effectively applied in the case of high temperature pressure gasification, for example, pressure gasification with liquid slag removal.

Far more effective is the application of the reaction in the presence of an inert charge, as in pressure gasification of solid fuel with dry ash removal.

In this connection and bearing in mind the purpose of our study, it was necessary to obtain experimental data on the velocity of the CH_4 + H_2O reaction under conditions favouring this process.

Experiments were carried out in the presence of a charge of fireclay pellets of 3-5 mm at temperatures of 500-1100°C, and pressures 1; 10; 20 and 40 atm, the ratios of $H_2O:CH_4$ in the blast mixture being 1; 5 and 10, and blast velocity, referred to a free cross-section under normal conditions, being 0.425; 1.06; 3.45 and 6 m/s.

Experiments were also carried out with a different nitrogen-content in the blast mixture. The height of the bed in all experiments was 500 mm. The experiments have shown that at temperatures above 800-850° with increased blast velocity (all other conditions being equal), the velocity of the CH_4 + H_2O reaction also increases, the degree of methane conversion, however, falls.

The degree of methane conversion when reacting with steam at various temperatures and pressures is practically independent of the $H_2O:CH_4$ ratio, i.e. the concentration of CH_4 in the blast mixture (Fig. 5).

Consequently, the reaction CH_4 + H_2O is a reaction of the first order under the conditions prevailing in the experiments.

This conclusion was substantiated by a series of experiments carried out at various temperatures, at a pressure of 20 atm, with a ratio of $H_2O:CH_4 = 5$, but having a different nitrogen-content in the starting gas (0-71.8% vol.)

The experimental data obtained enabled the effect of pressure variation on the course of the CH_4 + H_2O reaction at different temperatures to be determined.

The effect of this factor is shown in Fig. 6 - with increased pressure (all other conditions being equal) the degree of methane conversion increases.

The effect of pressure as found in the experiments must be regarded as an effect of the variation of two factors: the residence time of the gases in the reaction vessel and the reaction velocity constants.

With increased pressure the residence time of gases in the reaction chamber is prolonged and the apparent reaction velocity (the diffusion range or the boundary range in the kinetic regime) decreases.

The decrease in the apparent reaction-velocity constant with increased pressure proceeds more slowly than the increase in the residence time, which results in an observable increase in the degree of conversion.

The data relating to the velocity of the reaction CH_4 + H_2O in the presence of an inert charge have shown the possibility of achieving practically complete methane conversion, for example, at pressures up to 20 atm and temperatures in the range of 1100°; the methane concentration in the starting gas does not affect the rate of the process.

In conclusion, it must be stressed that the process of methane conversion with steam in a separate reaction vessel over an inert charge, agrees well with the basic industrial process of pressure gasification of solid fuels. It, therefore, becomes possible to simplify the design of gas cleaning equipment in the industrial plants. In addition, real possibilities exist for increasing the thermal efficiency of the entire process by utilizing the energy of the compressed high pressure gas in simple expansion turbines.

The favourable characteristics of the process described, encourage further work in this field.

Conclusions

1. Investigations were carried out with a view to obtaining gases having the required ratio of reactive components but with a minimum methane-content.

2. In order to determine conditions under which methane is formed during pressure gasification of solid fuel, experiments were carried out into the whole process of gasifying low-temperature peat coke with steam/oxygen mixtures of different ratios at pressures up to 50 atm, as well as the processes occurring in the reduction zone.

Experiments have shown the possibility of obtaining a gas under pressure having a predetermined ratio of reactive components. For each required pressure and desired content of reactive components a particular optimum blast composition is required.

An efficient method of restricting the formation of methane in pressure gasification of fuel consists in controlling the composition of the gas mixture entering the reaction zone.

3. An investigation into the conditions favouring the conversion of methane which has formed during pressure gasification of solid fuel has shown that when performing this reaction in the presence of coal, no worthwhile decrease in the methane-content in the gas is obtained.

An investigation into the reaction $CH_4 + H_2O$ in the presence of an inert charge has shown the possibility of obtaining practically complete conversion of methane at high pressure and at temperatures of the order of 1100°; the methane concentration in the starting gas did not affect the degree of conversion.

Controlling the methane-content of gas obtained in pressure gasification is most effectively accomplished in a separate apparatus in the presence of an inert charge; this agrees satisfactorily with the basic industrial process and enables the efficiency of the entire gas production process to be improved.

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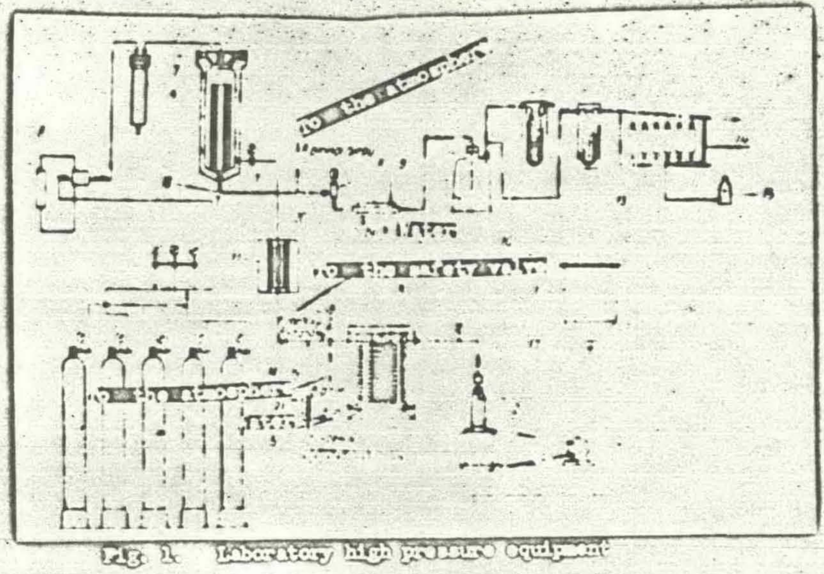

Fig. 1. Laboratory high pressure equipment

1 = tank, 2 = pump, 3 = steam boiler,
4 = gas producer, 5 = gas bottles, 6 = high
pressure flow meter, 7 = high pressure bandle,
8 = gas sampling probe, 9 = tubular condenser,
10 = condensed water tank, 11 = steam superheater,
12 = mercury pressure gauge, 13 = flow meter,
14 = series of pipettes, 15 = pressurised bottle,
16 = thermocouple, 17 = hydraulic valve, 18 = angle
valve 3/4", 19 = angle valve 1/2", 20 = angle
valve 1/4", 21 = coil condenser

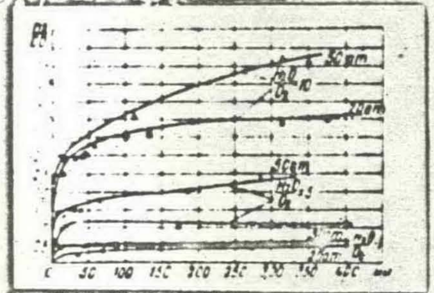

Fig. 2. Variation of the ratio H_2 : CO at different levels of the fuel bed when gasifying peat semi-coke under pressure with steam/oxygen blast of different compositions

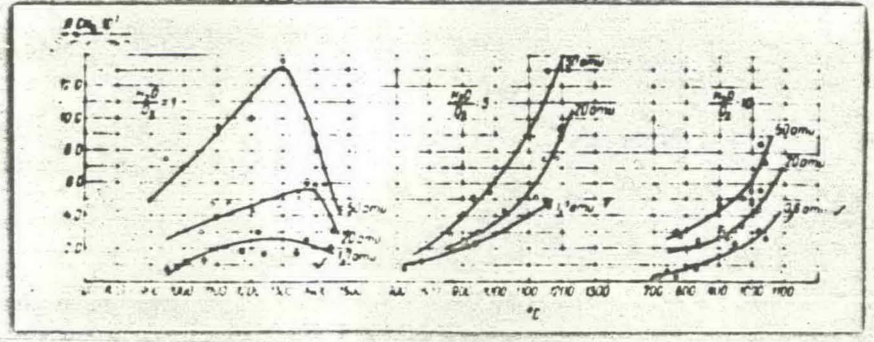

Fig. 3 Rate of methane formation when gasifying peat semi-coke under pressure

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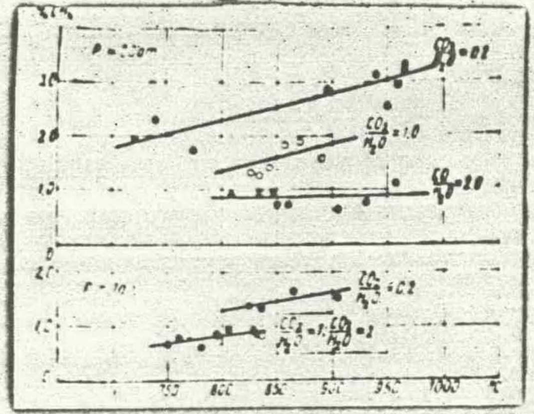

Fig. 4. Methane - content of dry gas obtained when reacting peat semi-coke with a mixture of Co_2/H_2O at difference temperatures and pressures

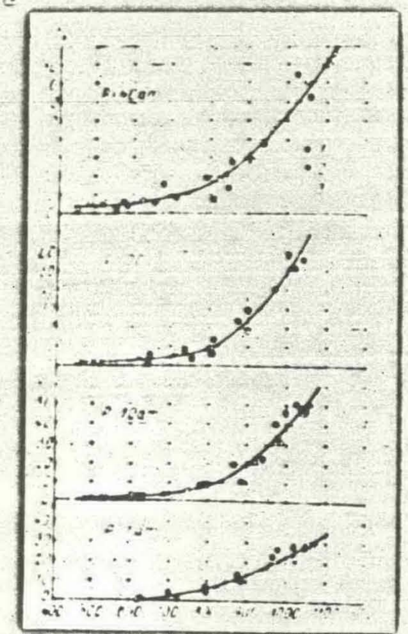

Fig. 5. Effect of temperature and blast composition on the degree of methane conversion with steam at different pressures (inert charge V = 0.425 m/s)

(1) $H_2O/CH_4 = 1$; (2) $H_2O/CH_4 = 5$;
(3) $H_2O/CH_4 = 10$

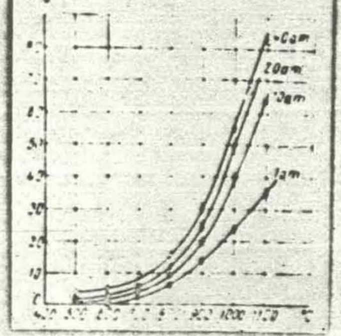

Fig. 6. Effect of pressure on the degree of methane conversion with steam at different temperatures (inert charge V = 0.425 m/s)