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STEAM REFORMING OF PROPANE OVER NICKEL-ALUMINA CATALYST

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ABSTRACT:

The aim of the present work was to study the steam reforming of propane at low temperature and atmospheric pressure. A commercial reduced nickel-alumina catalyst was used for all the experiments over a range of temperatures from 300-500°c. The primary object was to employ higher steam ratios at low temperatures in the catalytic steam reforming of propane in order to optimise Conversion and yield of the products. This was done in a packed bed reactor with continuous flow of both reactants. After condensing out the excess water the product gases were dried and analysed by infrared analysers and chromatographically.

INTRODUCTION:

The catalytic reforming of alkanes in the presence of steam has developed in the last forty years into one of the most important industrial process which provides different types of synthesis gas as well as a gaseous fuel.

For example, the process conditions can be modified to produce hydrogen for ammonia synthesis, hydrogen and carbon oxides for methanol synthesis and oxo reactions or a fuel gas which contains a high proportion of methane in addition to hydrogen and carbon oxides. The propane steam reforming reaction has been extensively investigated.

Aspects of propane steam reforming have been studied by a number of researchers (1,2,3).

It has been established by others (4,5), that when propane is reformed with steam over an active catalyst, the equilibrium product contains CH_4,H_2,CO_2,H_2O and CO.

The over all propane steam reforming reaction may be represented by the Stoichiometry:-(6,7)

$$C_3H_8 + H_2O = aCH_4 + bH_2 + cCO_2 + dH_2O + eCO$$

which when carried out over an active nickel catalyst gives very fast complete

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conversion of the feedstock with methane as the only surviving alkane in the product gas.

Thus, the reactions that occur when hydrocarbons are reformed are probably numerous and, with regard to those occuring initially, some what speculative. What ever the basic reforming reactions may be, several workers (1-5-12) are agreed that the reforming reactions quickly reach equilibrium over an efficiently active nickel catalyst, such as used in modern plants.

For the reforming of higher alkanes, such as propane it has been observed that, under typical reforming conditions, the only alkane present is methane and it is suggested that the higher alkanes undergo complete reaction with steam according to the following equations. (8)

$$C_mH_{2n} + mH_2O \text{ --------- } mCO + (m+n)\,H_2 \quad (1)$$

and

$$C_mH_{2n} + 2mH_2O \text{ --------- } mCO_2 + (2m+n)\,H_2 \quad (2)$$

The steam reforming of higher alkanes will then be described by either (1) and (2) together with reaction (3) and (4).

The equilibria which control the final gas product composition can be represented by the following two reactions (9,11).

Endothermic $CH_4 + H_2O <<=====>> CO + 3H_2$,

Exothermic $CO + H_2O <<=====>> CO_2 + H_2$

The first reaction, highly endothermic is pushed to the right thermodynamically, by increasing temperature and by a greater proportion of steam. It is pushed to the left i.e. against reforming only by increasing pressure. The second reaction exothermic is favoured to the right by decreasing temperature and by a greater proportion of steam, but to the left by increasing temperature. Pressure has no effect on it. For the two reactions to proceed together a temperature between those which give optimum conversions is being studied experimentally. This article contains the results obtained with the over-all reaction for a range of temperatures and the effect of various steam ratios on the product gas composition.

The wet product gas compositions were calculated from the dry product gas composition (experimental results) and knowledge of the propane steam feed ratio.

EXPERIMENTAL EQUIPMENT AND PROCEDURE FOR STEAM REFORMING.

A flow of the experimental facility designed, built and operated in the present work to study propane steam reforming is shown in figure 1. The apparatus employed in this work was designed in such a manner that the equipment could accommodate a large range of experimental conditions. The reactor was of a fixed bed tubular type and constructed of stainless steel tube, 23.0mm O.D. and 1.22m long. All the experiments were carried out using a CRG type catalyst (3.2mm dia x 3.2mm L) containing 75% nickel on a y-alumina support which also contained traces of alkali. A catalyst mass of 0.109 kg and 203mm bed length was used to carry out the reforming experiments. This catalyst was supplied by the British Gas Corporation. Before using fresh or

regenerated catalyst for the reforming reaction, a reduction (activation) schedule was always followed in order to reduce the nickel oxide to matallic nickel. In some cases commercial catalysts contain traces of residual sulphates, which must be removed by reduction with hydrogen in the presence of steam before full activity can be achieved. The reactor tube operated in the vertical position. Water was fed from a glass burette (500ml), by a microfeed pump and different flow rates of water were achieved by choosing different output positions on the micrometer of the pump. High purity hydrogen, propane and Nitrogen were obtained from cylinders. After pressure reduction by means of regulators, the gases were metered with rotometers within the range 200ml-900ml/min. They then passed through the evaporator furnace. The liquid water was fed by a microfeed pump through the capillary tube into the vaporiser maintained at $100^{o}C$ - $250^{o}C$ where the water evaporated. This homogeneous mixture of propane steam was then passed into the reactor.

After the propane steam mixture was fed to the reactor, the reforming reaction was allowed to continue at a constant temperature for about one and a half hours to ensure steady state operation. On leaving the reactor tube, the reaction products passed into a water cooled co-current condenser for separation and collection of unreacted steam. This wet gas stream was then passed through a drying tube which contained silica gel(self indicating). After drying, the dry product gas was then split into two streams, one of which led to the infrared gas Analyser, while the other passed into the sampling valve of the gas chromatograph. Sampling started immediately after the reaction began and continued at regular intervals. The system wss deemed to have achieved a steady state when the exit concentrations of CO, CO_2, and H_2 became constant. The concentrations of CO and CO_2 were directly measured from infrared gas analysers. The hydrogen and methane concentrations were found by a mass balance. Initially the hydrogen and methane were measured by means of the gas chromatography. All connecting lines were constructed from stainless steel and copper tubes with the exception of the glass burette for the water feed and the glass tube containing silica gel for drying the gas samples to be analysed. Temperatures were recorded in the reactor by a moveable chrome alumel thermocouple (diameter 1.00mm) and in the pre-heat furnace by another chrome-alumel thermocouple of the same diameter. Connections from both terminals to the indicator were made with compensating cables. The reactor thermocouple was situated in the thermo-well within the reactor and could be positioned at any height of the catalyst bed, thus permiting the internal temperatures to be scanned. The reactor tube had two windings, one on the preheating section in the upper part of the reactor, while the other was wound alongwith the catalyst bed section.Both were wrapped with electrical heating tape and insulated with glass fibre and Lamella mat. Nitrogen (pre-purified grade, minimum purity 99.998%) was used during the warmup period, and also to purge the system when shutting down.

RESULTS AND DISCUSSIONS

A feature of the steam reforming of propane shows the virtual absence of any alkane in the product stream. Instead, all propane was converted to a greater or lesser extent to methane and oxides of carbon.

Results for the compositional variation of the product gases as a function of temperature and for different values of the propane steam ratios are given in figures 2 to 4.All temperatures are those of the reaction product gas composition from the reactor. The following ranges of parameters were used for propane steam reforming in the temperature range 300-500^{o}C. Propane steam molar ratios of 1:6,1:10,1:15.5, (figures 2 to 4).

The influence of the operating steam ratio is given in figures 2 - 4 where the experimental reformed dry gas composition are plotted against temperature and show its major influence.

As the temperature increases above 300^{o}C the concentration of methane falls with respect to temperature, while all reformed reaction products also increase simultaneously, throughout the temperature range. The rate of increase for carbon dioxide is slower, however, than for hydrogen. It can also be observed from figure 2 that at a temperature of about 448^{o}C the concentration of methane is approximately equal to that of hydrogen. Where as in the same figure at a temperature of about 349^{o}C the concentration of carbon di oxide is equal to that of hydrogen. This effect is shown in all figures. Because of the sign variation of the standards free energy change of the water gas shift reaction (eauation 4) with temperature, at low temperature the equilibrium will favour the formation of carbon di oxides while in the high temperature region, the equilibrium will be shifted in the direction of carbon monoxide formation. An examination of figures 2 - 4 shows that with increasing steam propane feed ratio this "crossover" temperature decreases for both pairs (H_2 over CH_4 and CO_2 over CH_4) for low temperatures.

In general, figures 2 to 4 show that with increase in temperature the amount of methane decreases in accordance with the thermodynamics of reaction (3). A corresponding increase in production of hydrogen occurs with increase in temperature together with a slight increase in carbon dioxide and carbon monoxide.

It can also be seen from figure 2 to 4 that an increase in the steam propane ratio gives rise to an increase in the production of hydrogen and carbon dioxide, emphasising the effect of the water gas shift reaction (equation (4) above). Increase in the steam propane ratio also gives a higher conversion of methane.

This is because of the high proportion of steam in the reaction, which converts some of the carbon monoxide into carbon dioxide, and decreases the concentration of carbon monoxide in the product gas composition.

Thus for maximising the production of hydrogen with maximum conversion of

methane, a high steam propane ratio should be used. These results are consistant with equilibrium being approached in the reaction bed.

CONCLUSIONS:

The following conclusions can be drawn from the present study:-

The analytical results obtained from this study can be used for material and energy balances, in the design and operation of a propane steam reforming plant. These results are particularly useful for quick adjustments of steam to propane ratio and reactor temperature in order to fix the out-let gas composition. The results obtained for propane steam reforming show that the product gas composition on a wet basis does satisfy the equilibrium constant K1 for methane-steam reaction and K2 for water gas shift reaction, over the range of temperature from 300-500^{o}C for all the steam ratios employed in the propane steam reforming. It is fully appreciated that the experimental results for product gas composition on a wet and dry basis as presented in table 1 and 2 can be used for a given c/steam ratio in a feed stock and to fix the out-let gas composition.

In the propane steam reforming as the steam ratio incrases at a given temperature, the carbon monoxide and methane concentrations decrease while hydrogen and carbon dioxide concentrations increase in the product gas composition (10).

The temperatures and higher steam ratios have similar effect on the propane conversion.

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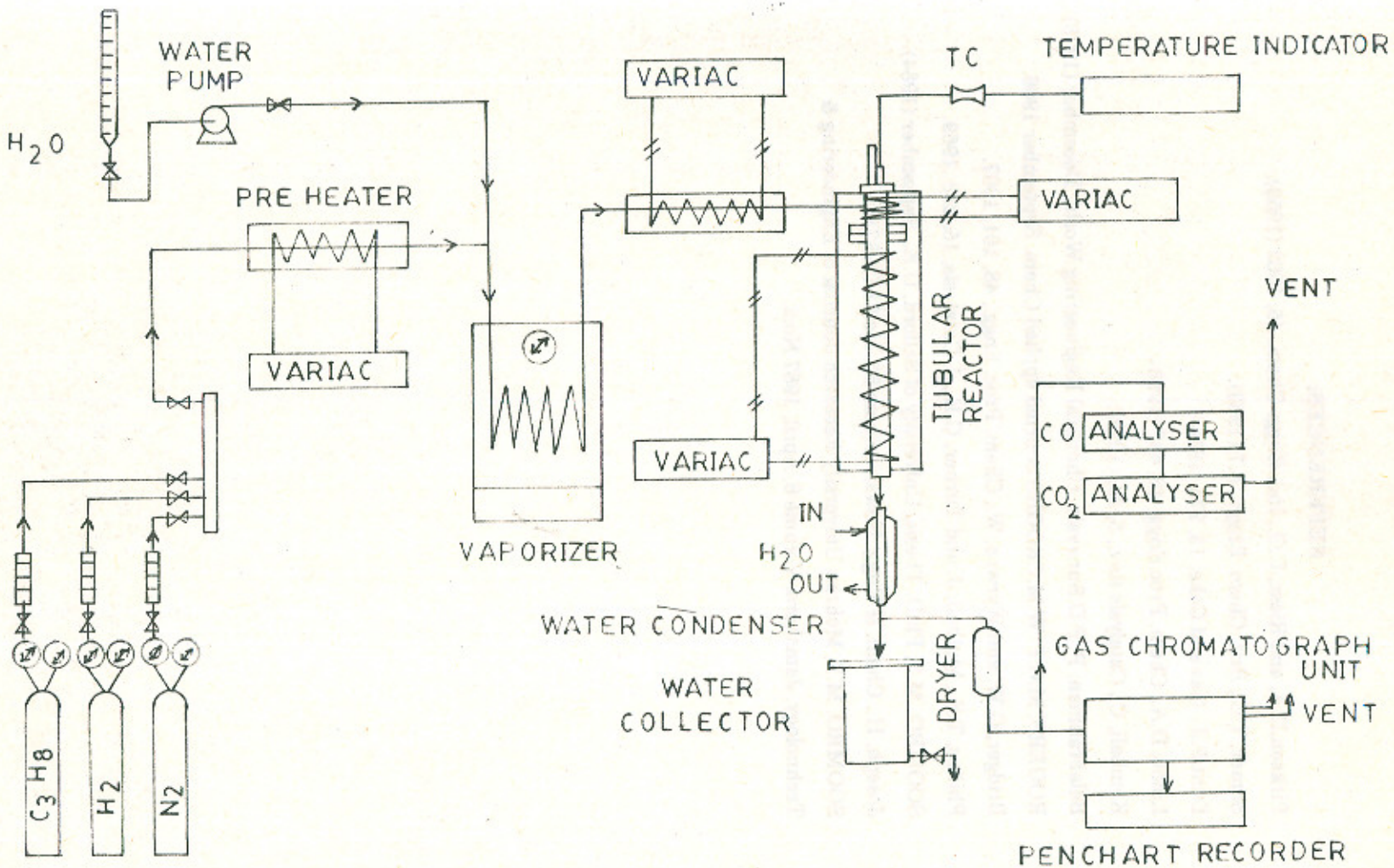


Fig. 1. SCHEMATIC DIAGRAM OF THE REFORMING APPARATUS

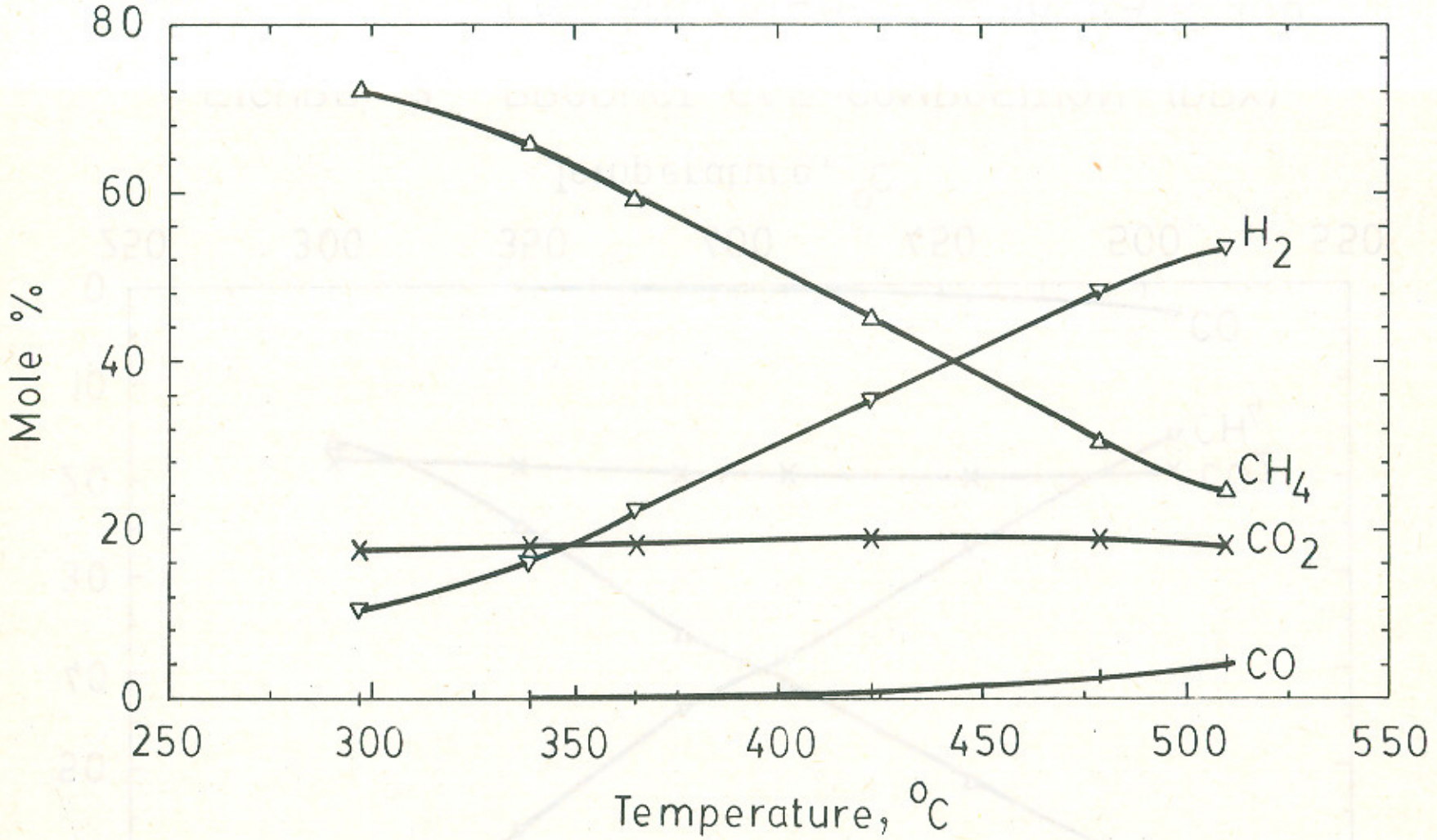


FIGURE: 2. PRODUCT GAS COMPOSITION- (DRY)

PROPANE- STEAM MOLAR RATIO 1:6

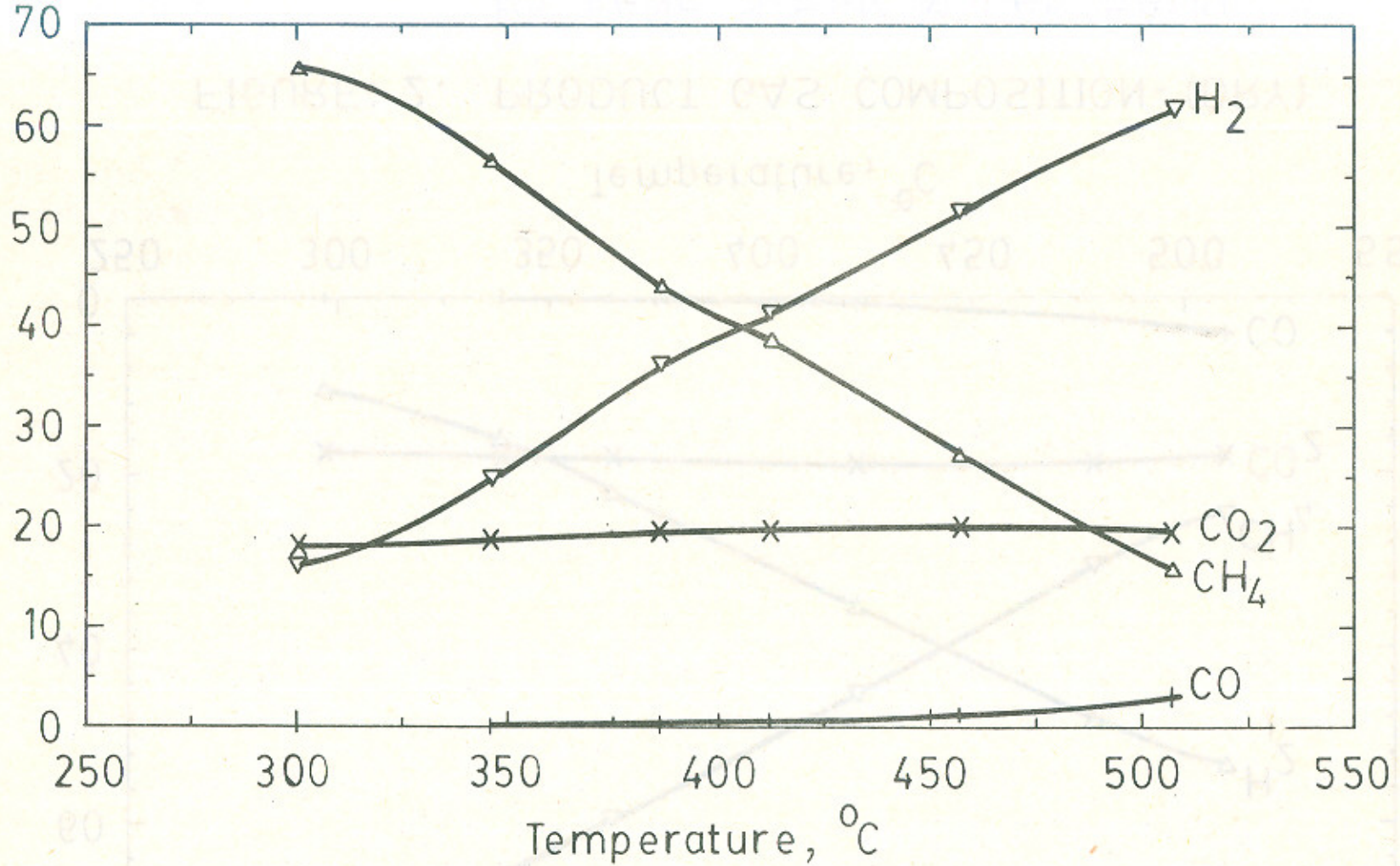


FIGURE : 3. PRODUCT GAS COMPOSITION - (DRY)
PROPANE - STEAM MOLAR RATIO 1:10

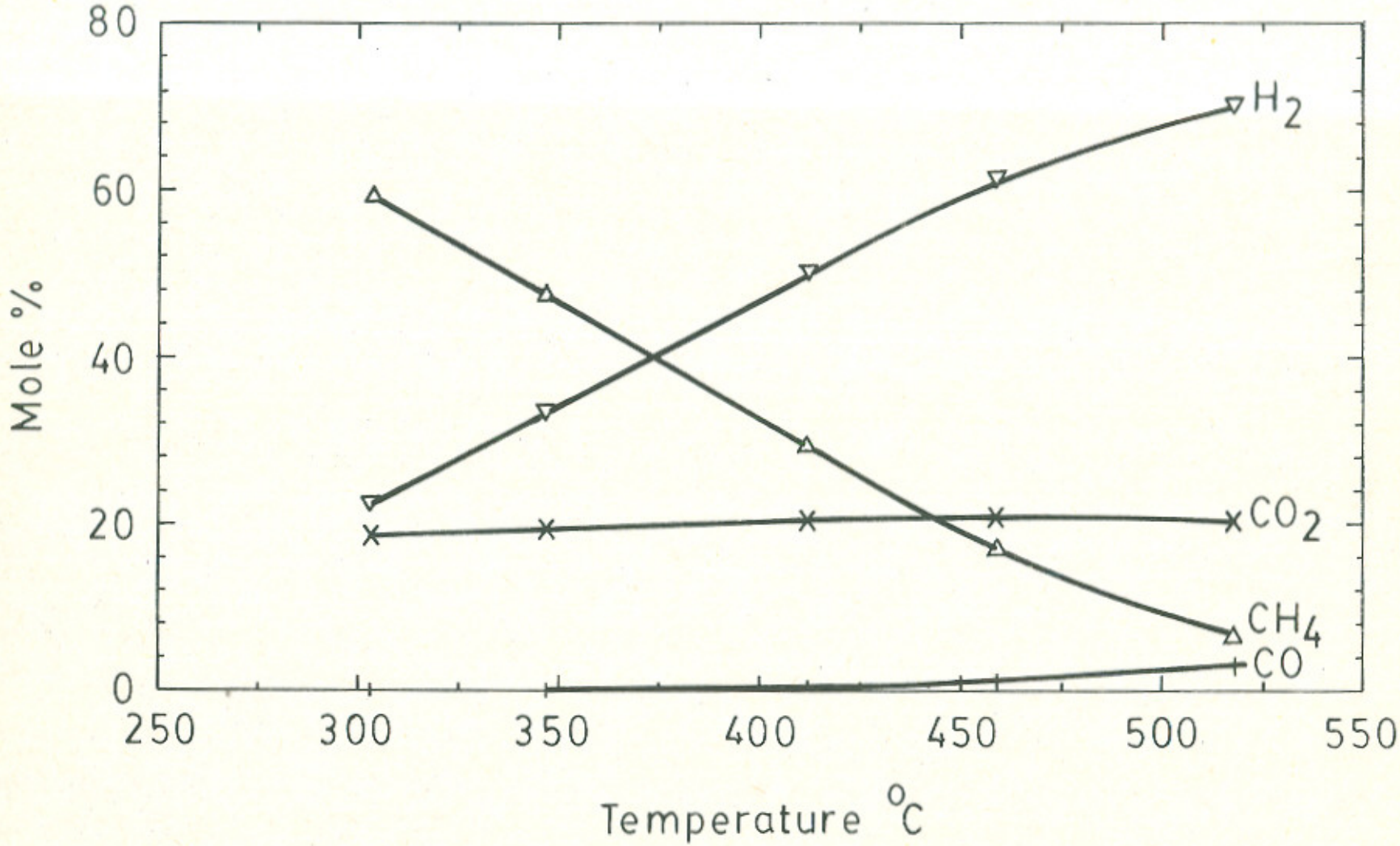


FIGURE : 4. PRODUCT GAS COMPOSITION - (DRY)

PROPANE - STEAM MOLAR RATIO 1:15.5

