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Catalysis Today 24 (1995) 289–291

CATALYSIS TODAY

Conversion of natural gas to liquids and hydrogen in a thermal diffusion column TDC reactor

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Abstract

The conversion of natural gas to aromatic compounds and hydrogen using a thermal diffusion column reactor has been examined at different modes of operation and reaction parameters. Practically complete natural gas conversion has been obtained.

1. Introduction

The direct unoxidative conversion of natural gas (NG) to liquid hydrocarbons is limited by the thermodynamic equilibrium. Below 1000°C the equilibrium is on the CH_4 side for benzene formation:

$$6CH_4 \leftrightarrow C_6H_6 + 9H_2 \quad (1)$$

At 1077°C the free energy for this reaction is equal to zero [1] and CH_4 conversion to benzene is estimated as 57%. It appears that a limit of 20% yield of liquid is being approached for a methane pyrolysis in a conventional reactor including a catalytic process [2,3] at 1100–1200°C.

The thermal diffusion column (TDC) is a promising method to increase a yield of liquid products. The TDC reactor is a non-equilibrium system with H_2 separated from hydrocarbons by convectional currents.

The 1941 work of Hirota [4] was recently repeated by Yamaguchi et al. [5,6]. Hirota produced an oil when methane was passed over a heated vertical tungsten wire in a TDC reactor. Yamaguchi et al. [6] showed that in the downward flow of CH_4 over the heated filament ethylene was the major product, i.e. no oil was formed. The oil produced in the upward flow showed a 50% yield with a 55% conversion of methane.

We have since determined the composition of the oil [7] but due to the GC/MS inlet configuration we missed the main most volatile products, namely benzene and toluene.

In the current investigation we have examined the effects of the wire temperature, the variation in the angle of the reactor from the vertical to almost horizontal, the upward and downward flow on the natural gas conversion, and the composition of products. The experiments were conducted in order to obtain a high natural gas conversion.

2. Experimental

The experiments were performed in a water cooled tubular Pyrex reactor of 2.0 cm ID with Pt or W wire of 0.2 and 0.25 mm diameter centrally located in the reactor. The NG (97.7% CH_4, 2.1%

SSDI 0920-5861(95)00046-1

C_2H_6, 0.1% C_3H_8) was introduced to the reactor and products were analyzed by GC and GC/MS methods. The temperature of the wire was measured pyrooptically.

3. Results and discussion

For the upward flow of NG the ethane conversion to ethylene was observed at the wire temperature of 700°C. The methane conversion occurs at 850°C, the benzene was found in the reaction products and the drops of liquid were condensed on the cooled walls. At 950°C the ethylene concentration was maximal, while the benzene and toluene concentration increased with increase in the temperature. A high NG conversion and a permanent flow of liquid to the bottom collector were found at a T_w higher than 1000°C. At the temperatures above 1150°C the reaction was complicated by the coke formation on the walls and acetylene was found in the gas products. The dependence of methane conversion on the wire temperature is shown on Fig. 1.

The liquid obtained in the trap installed after the reactor consisted primarily of benzene, while the liquid from the bottom collector was a complex mixture of benzene, toluene, xylenes, naphthalene and minor quantities of polynuclear aromatic compounds.

Using a 40-cm long Pt wire, we obtained a methane conversion of 55% under 300 Watts and

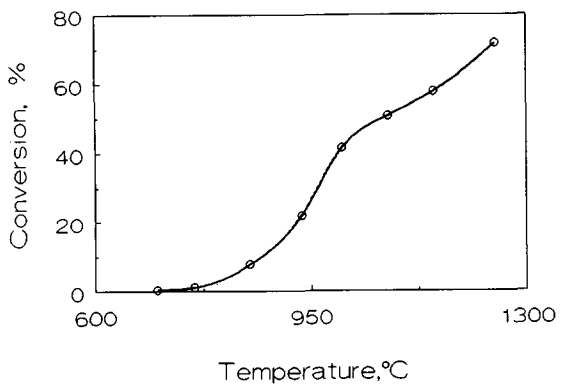

Fig. 1. Methane conversion as a function of temperature. Pt wire 40 cm long, 0.2 mm diameter, feed flow-rate of 13.9 L/h.

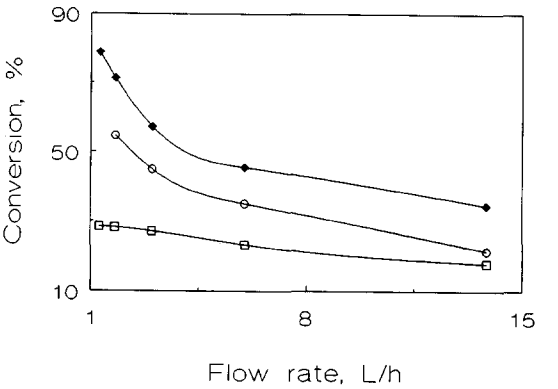

Fig. 2. Methane conversion versus flow-rate for different modes of operation. Pt wire 40 cm long, 0.2 mm diameter, power 280 Watts. (♦) Upward flow, 90°; (○) upward flow, 45°; (□) downward flow.

30 ml/min of the feed flow-rate. For 8 hours we converted 5.2 g of methane passed. By following a stoichiometric course, this amount of methane are converted to 4.2 g of benzene or 4.3 g of naphthalene. We collected 3.8 g of liquid (0.5 g in the trap, 2.7 g in the collector, 0.6 g on the walls). The liquid obtained in the collector contained 38% benzene, 9% toluene, 10% xylenes, 5% indene, 31% naphthalene and 7% heavy polynuclear compounds (mol.-%).

With an increase in the temperature and the contact time, the concentration of heavy products in the collector liquid obtained markedly increased. At low temperatures and low NG conversion traces of dienes and trienes were found in the liquid. These products are probably the intermediates produced by ethylene polymerisation and are converted to aromatic compounds.

When the reactor was set at a 45° angle, liquid removal to the collector was favoured under the upward flow system, while in the near horizontal mode liquid was not removed from the reactor which results in the formation of heavy hydrocarbons.

For the downward flow the yield of ethylene increased to 9% in comparison with upward flow (maximal value of 4.5%) and the liquid from the collector contained basically BTX fraction. But downward mode requires significantly more energy consumption due to the lowering of the

Table 1
The conversion of natural gas in the TDC reactor, upward flow mode.

N	Conditions	Power, Watts	T_w, °C	Flow, mL/min	Exit gas composition		
					H_2	CH_4	C_2H_4
1	Pt wire 80 cm	750	1185	200	97,0	3,0	0,05
2	W wire 2*80 cm	1180	1080	200	99,6	0,4	0,03

* two consequently connected TDC reactors

thermal diffusion effect. At higher flow-rates the conversion of NG is reduced, especially for the upward flow mode. The dependence of methane conversion on the feed flow-rate for the different modes of operation is shown on Fig. 2. Using a Pt wire the energy required is lower than for W wire, but the coke formation on the wire leads to unstable conditions.

The series of experiments were carried out in order to obtain a high natural gas conversion. The best results are shown in Table 1.

One can see that practically complete NG conversion was obtained and the exit gas contained practically pure hydrogen. The use of multicolumn reactor looks more attractive because it is possible to carry out the reaction at the lower wire temperature that reduces the coke and heavy products formation. In addition the liquid obtained in the second reactor contained more BTX fraction owing to the presence of hydrogen that prevents the polymerisation of liquid. While for the first experiment, Table 1, the ratio of BTX fraction to heavy products (including indene and naphthalene) was only 0.31, for the first collector (second experiment, Table 1) that ratio was 0.72, and for the second collector the ratio was 1.33.

Based on the benzene formed and the electrical energy used it is estimated that the conversion efficiency is only about 2%.

4. Conclusion

The above results show the potential of TDC reactors. Complete natural gas conversion has been obtained, but further improvements are necessary to decrease energy consumption.

5. Acknowledgements

We are grateful to EMR and NSERC for supporting this work.

6. References

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