Note

Chromatographic pulsed micro-reactor system for studying the kinetics of hydrocarbon conversions

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The use of a pulsed micro-reactor system together with gas chromatography in quantitative studies of chemical kinetics has been common in recent years, and the comparative merits of micro-reactor systems, including the pulsed system, have been described by Ettre and McFadden[1]. Quantitative and reproducible sample-injection techniques have been described[2–6] and a dual-channel pulsed micro-reactor system has been reported recently[7]. This paper describes the development of a micro-reactor system that has yielded good results for two difficult reaction systems, namely hydrocarbon oxidation and hydrocarbon cracking.

In the study of the kinetics of gas-phase hydrocarbon oxidation, a continuous packed-bed integral micro-reactor would be very convenient but for the following difficulties. (a) Pre-heating of the hydrocarbon–oxygen mixture would not be possible as the reaction would start before the reaction zone was reached; only the oxygen (or air) can be pre-heated. Even then, when the hydrocarbon feed mixes with the oxygen (or air) at the entry of the reaction zone, an uncontrollable increase in temperature due to ignition could occur above 650°[8]. (b) Even under conditions when pre-ignition is not possible, the maintenance of isothermal conditions in the reaction zone would be doubtful.

A pulsed micro-reactor system would be more rigorously isothermal if only a small sample of hydrocarbon–oxygen mixture were pulse-fed to a pre-heated inert gas stream entering the reaction zone. With the system developed in this work, studies on the kinetics of the stoichiometric combustion of liquefied petroleum gas (LPG, a mixture of ethane, propane and butane) in a packed-bed micro-reactor (catalytic and non-catalytic) have been conveniently accomplished up to 800°.

In studies on the kinetics of cracking, an empty tubular reactor is usually used, which is not amenable to integral plug-flow analysis. If a packed-bed micro-reactor is used as a continuous reactor, a steady state is never achieved because of formation of carbon in the packed bed. Pre-heating is also not possible before the reaction zone. The use of a pulsed micro-reactor for such a study of thermal cracking would be very convenient, although there is not much evidence of this in literature. Using the system developed in this work, the kinetics of the thermal cracking of LPG have been studied successfully up to 850°, with more than 85% conversion within prescribed residence time limits of industrial reactors. The results of these studies will be presented elsewhere[9,10].

The experimental arrangement, shown in Fig. 1, is similar to those used by other workers, with the following exceptions. The carrier gas is split into two unequal streams in the ratio of approximately 95:5. The larger stream passes through the pre-heating zone and mixes with the unheated smaller stream just before the reaction zone. The smaller stream, before entering the reactor, passes through a sampling valve, and in the process picks up a slug of reactant from the sample loop whenever necessary. The reaction takes place under dilute conditions, the maximum concentration never exceeding 5%; the cooling effect by the 5% stream at the entry of reactor is neglected. The exit of the reactor is a water-jacketed tube that extends up to the bottom of the packed bed. It is assumed that the reaction stops as soon as the product gas enters the cooled outlet tube. The product gas is split into two portions. one of which passes directly to the detector system to trace the pulse shape through the reactor and the other passes through the chromatographic column for separation of the components.
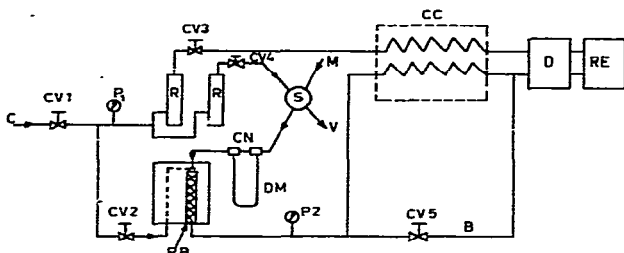

Fig. 1. Flow diagram of experimental system. B = column by-pass; C = carrier gas; CC = chromatographic column; D = detector; CN = constriction; CV = control valves; DM = differential manometer; M = reactants: P1, P2 = pressure gauges; R = rotameters; RB = reactor bed; RE = recorder; S = sampling valve; V = vent.

The reactor (Fig. 2) is a rectangular block of stainless steel with four parallel holes, two of which are suitably connected to make it one reactor of a twin set. Fig. 1 indicates only half of the reactor block. The reactor block is heated by placing it completely inside a radiation furnace heated by electrical resistance. The first hole in the reactor (suitably packed) acts as the pre-heater, and the second hole, nearer the centre of the block, acts as the reactor. The connections outside are made through thin-walled tubes welded to the block in the hot zone, the other ends outside being connected through water-cooled gland fittings. Suitable temperature-measuring pockets for inserting thermocouples are drilled into two opposite ends of the reactor block. This design of the twin reactor block has been tested extensively for operation up to 850°, which is the operating limit of the stainless-steel material (AISI-304) used.

To start a run, the carrier flow is adjusted to a suitable value, and the chromatograph and recorder are brought into steady-state operation. The reactor is then slowly heated. One sample is injected at about 300–350°, and is taken as the unreacted sample standard. Then the reactor is adjusted to a constant reaction temperature and the results of a number of sample injections are recorded, before adjusting the reactor to another temperature. In one set of runs the flow-rate is kept constant and the temperature is varied, and in another set the flow-rate is varied.
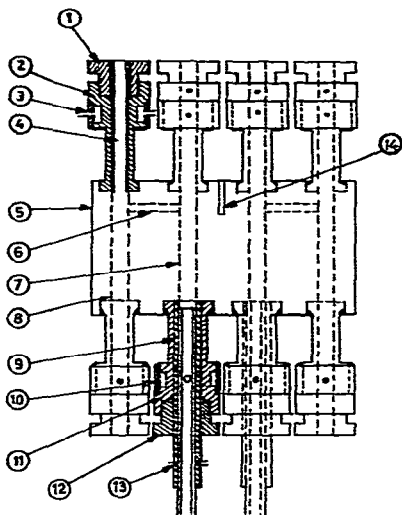
Fig. 2. The pulsed micro-reactor (stainless steel AISI 304). 1 = Gland nut; 2 = gland joint; 3 = cooling for gland joint; 4 = connecting tube to the reactor body; 5 = main reactor block; 6 = connection between pre-heating zone and reaction zone; 7 = reaction zone; 8 = pre-heating zone; 9 = cooled outlet tube; 10 = cooling for gland joint; 11 = outlet gland joint; 12 = gland nut; 13 = cooling water connection; 14 = thermocouple position.

Fig. 3 shows a typical recording from an LPG combustion, the hydrocarbon peaks being detected with a flame-ionization detector. Nitrogen was used as the carrier gas, and the LPG–oxygen mixture was fed through a sampling valve (0.5 cm^3). The first peak is the shape of a reactant pulse recorded as a measure of the total hydrocarbons present, while the other four peaks are constituent hydrocarbons of LPG. From the first peak of the reactant pulse and the product pulse, the kinetics can
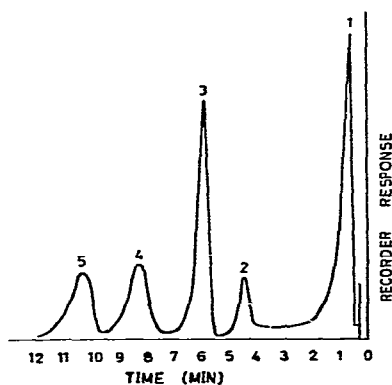

Fig. 3. Recorder trace for a typical pulsed micro-reactor run for combustion of LPG in an inert packed bed. Column, 6 ft. × 1/8 in., 15% squalane on Chromosorb P (80–100 mesh). Column temperature, 50°; flame-ionization detector; carrier gas, nitrogen at a flow-rate of 40 ml/min. Peaks: 1 = total hydrocarbons (pulse shape); 2 = ethane; 3 = propane; 4 = isobutane; 5 = n-butane (peaks 2–5 represent the detailed hydrocarbon composition of the product or reactant).

be evaluated in terms of the disappearance of total hydrocarbons. From the component peaks, the detailed kinetics can be evaluated in terms of the disappearance of individual hydrocarbons; the combustion products were not analyzed in this case. However, they can be analyzed by using helium as the carrier gas and a thermal conductivity detector.

Fig. 4 shows the results of a cracking run; Fig. 4a refers to the unreacted sample and Fig. 4b to the products after cracking.
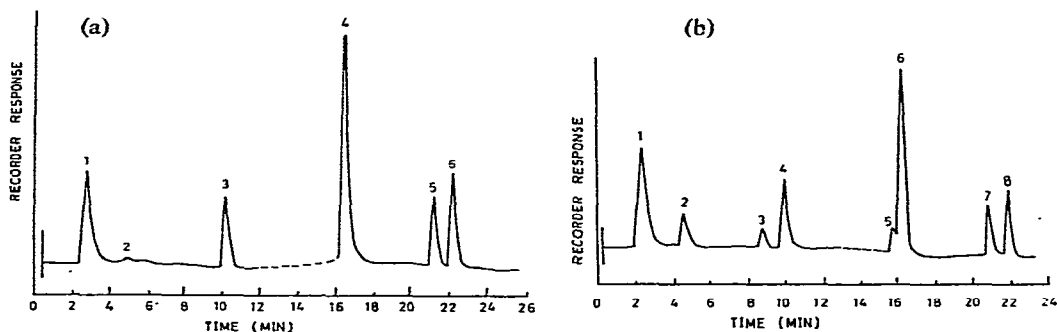

Fig. 4. Recorder trace for typical LPG cracking runs (in excess hydrogen). Column, 10 ft. × 1/4 in. O.D. Porapak Q; column temperature, initial 65°, final 200° at a programming rate of 8°/min; thermal conductivity detector; carrier gas, hydrogen at a flow-rate of 30 ml/min. (a) Peaks: 1 = total hydrocarbons (pulse shape); 2 = methane; 3 = ethane; 4 = propane; 5 = isobutane; 6 = n-butane (peaks 2–6 represent the detailed hydrocarbon composition of the reactants). (b) Peaks: 1 = total hydrocarbons (pulse shape); 2 = methane; 3 = ethylene; 4 = ethane; 5 = propylene; 6 = propane; 7 = isobutane; 8 = n-butane (peaks 2–8 represent detailed hydrocarbon composition of the product or reactants).

Detailed kinetics have been evaluated for the cracking of LPG using this system. The system, with some modifications, is currently being extended to studies of the cracking kinetics of liquid hydrocarbons.

ACKNOWLEDGEMENT

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