Novel Microreactor with Quench System for Kinetic Study of Propane Pyrolysis

A novel microreactor with a rapid direct quench system was developed to study fast hydrocarbon pyrolysis reactions. Heating of reactants inside the reactor was achieved by a Curie Point Pyrolyser. The propane pyrolysis reaction was studied at four different temperature levels: 600, 700, 800 and 900°C. Pyrolysis times were varied from 0 to 2 s between 600 to 800°C and from 0 to 1 s at 900°C. The primary reaction products were methane, ethylene, hydrogen and propylene. Using a developed and very effective quench technique increased the production of olefins and reduced the formation of methane. A first-order kinetic analysis performed on the experimental data between 600 and 700°C yielded an activation energy of 216 kJ/mol, which is in the range of other researchers.

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Introduction

The study of fast pyrolysis reaction kinetics at elevated temperatures requires the control of important variables, such as heating rate (temperature rise time), contact time, quench time, and reaction temperature. The most important factor that affects the pyrolysis reaction is the temperature-time profile which is a characteristic of the pyrolysis reactor. Since construction of a pyrolysis reactor at first thought appears to be a simple task, it has resulted in many workers designing their own units. Easy handling of the sample, rather than control of the pyrolysis process, has been the guideline in the design of most of these units. As a result, interlaboratory reproducibility has suffered badly.

The objective of this work was to develop a microreactor with a direct contact quench system that permitted the study of the kinetics of fast hydrocarbon pyrolysis reactions. This new reactor allowed careful control and measurement of the temperature profiles experienced by the reactants. The propane pyrolysis reaction was chosen since much has been published on this subject and would hence help in the comparison of the results. Not being a complex molecule, propane is an excellent choice for the study and comparison of product distributions.

Equipment Selection

All the pyrolysis units described so far in the literature can be classified into two major groups according to their mode of operation: pulse mode units and continuous mode units. All the pyrolysis units in which thermal energy is supplied as a "pulse," giving rise to temperature-time profiles similar in shape to a half square wave, are classified as pulse mode units. For example, pyrolysis units based on high frequency induction heating, radiation, dielectric discharge and arc come under the category of pulse mode units (Levy, 1966, 1967). A tubular reactor is a classic example of a continuous mode unit. Typical temperature-time profiles of a pulse-mode unit and a continuous-mode unit are shown in Figure 1.

Precise kinetic studies on pyrolysis reactions require a pyrolysis device with a zero temperature rise time and a zero quench time. Since such an ideal temperature profile is not achievable, other temperature profiles generated by different pyrolysers are examined. A pyrolyser can then be selected and modified to produce a temperature profile that can best approximate the ideal temperature profile.

Pyrolysis in externally heated tubular reactors has been the favourite choice of many workers. However, the temperature profile of a typical tubular reactor is quite different from the ideal profile as shown in Figure 1. The basic problem in using a tubular reactor is that the temperature profile is a function of the flowrate and position in the reactor. In these reactors, the temperature profile changes for different residence times and hence, is not acceptable when an accurate kinetic analysis is required.

An additional problem is that the reactant temperature is not the same as the reactor-wall temperature. The customary practice of measuring the temperature of a gas flowing inside an externally heated tube is to insert a thermocouple directly in the

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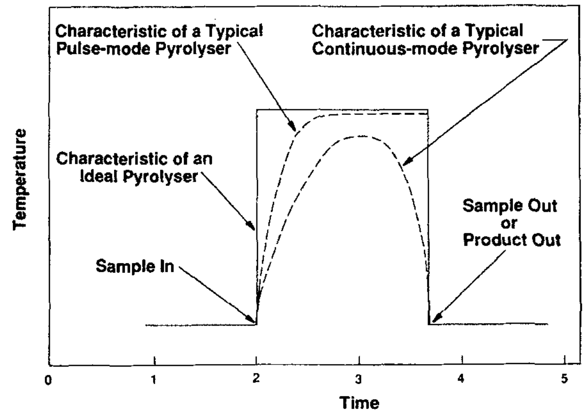

Figure 1. Temperature profiles of various pyrolyzers.

reactor space. Such practice gives consistently high readings due to radiation from the tube wall. Since the magnitude of the error thus introduced varies with the rate of flow, it is impossible, when varying the time of contact, to maintain constant temperature by means of an inserted thermocouple. The temperature recorded can be 25 to 85°C higher than the actual reaction temperature (Haslam and Chappel, 1925; Seebold, 1985).

One of the main problems encountered in the derivation of rate equations from experiments in tubular reactors is the longitudinal temperature profile. There is no sharp distinction between the preheat, reactor and the quench sections. The concept of equivalent reactor volume was introduced by Hougen and Watson (1947) to correct for the nonisothermality of the tubular reactor. Hougen and Watson suggested that this method should be used for small temperature differences. They also warned that this method is subject to errors whenever several reactions occur simultaneously with different activation energies. The temperature gradients existing in a tubular reactor can be quite large. Also, pyrolysis is composed of scores of free radical reactions with very different activation energies. Hence, the equivalent reactor volume concept cannot be applied with reasonable accuracy to the study of pyrolysis reactions taking place in a tubular reactor. Therefore, the varying nonisothermal profile generated by continuous-mode pyrolysis units is not recommended for the study of pyrolysis kinetics.

Pulse-mode units belong to one of the following subgroups: shock-tube, laser, arc, filament-resistive heating and high-frequency induction heating. Although the temperature rise times of the shock-tube, laser and arc pyrolysis units are shorter than other units, the determination and verification of the equilibrium pyrolysis temperature is a serious problem. In shock-tube reactors, there is an error of 5 to 10% in determining the residence time and temperature determination is rather inaccurate (Bradley and Frend, 1971). In laser, arc or plasma jet pyrolysers, the reaction temperatures are very approximate. Since the pyrolysis temperature is the key variable in the study of reaction kinetics, these units should not be used for quantitative work.

The filament pyrolysers use a filament made of platinum. The reactant sample is directly applied onto the platinum foil. An older technique involved an applied voltage at the ends of the platinum foil resulting in an increase in the temperature due to resistive heating. A variation of the technique developed by Levy (1967) is based, in principle, on applying relatively high voltage to the terminals of the filament and rapidly decreasing its magnitude to the normal level, thus performing a "voltage sweep." This results in a rapid rise of the filament temperature to approach pyrolysis temperatures without reaching the melting point of the filament. Under such conditions, the temperature-time profile approaches the ideal "square wave" shape.

There are, however, some disadvantages to filament units. Filament geometry has a paramount influence on the heat dissipation from the filament. Large differences in temperature can be expected along the filament (Levy 1966). The hot and cold spots become an important discouraging factor in pyrolysis studies. Since the same filament is used repeatedly, carbon being dissolved in the platinum foil changes its characteristics (Jennings and Dimick, 1962). Further, the changing resistivity of the filament changes the equilibrium temperature of the filament. For quantitative pyrolysis studies, temperature profiles, which are a function of the previous history of the filament are not acceptable.

Induction heating in a Curie Point Pyrolyser is a pyrolysis technique that consists of application of high frequency induction heating to a sample in contact with a ferromagnetic conductor. The temperature of the conductor rises in a few milliseconds to its maximum temperature known as the Curie Temperature and then remains constant. Curie Point Temperature is the temperature at which a ferromagnetic material loses its ferromagnetism and is dictated by the composition of metal. When a ferromagnetic material is placed in an induction coil and the coil is energized with direct current, the material becomes magnetized. When the polarity of the current is changed, the magnetic poles are reversed. If the polarity of the coil is changed rapidly, hysteris heat is generated in the ferrous material due to the friction of the changing polarity. Self heating will cause the ferrous material to very rapidly reach a temperature at which it loses its magnetism. It then maintains this temperature. By selection of the appropriate ferromagnetic alloy, a wide range of conductor temperatures, and therefore pyrolysis temperatures, can be obtained.

Induction heating in a Curie Point pyrolyser approaches the ideal "square" temperature-time profile. The advantage of this pyrolysis device over other pyrolysers is that the final temperature (Curie temperature) depends only on the ferromagnetic material and is independent of any fluctuations in experimental conditions (Buhler and Simon, 1970). Also, catalytic effects have not been observed when using ferromagnetic conductors of different composition (Jones and Moyles, 1961). Pyrolysis results were not changed by coating the conductors with gold or platinum (Simon et al., 1967).

Dynamics of Microreactor System

The system consisted of a Curie Point pyrolyser, microreactor with quench system, timer control unit, and the analysis equipment. The Fischer Model 0316 Curie Point pyrolyser used in this study consists of a pulsing control unit, a solenoid valve and a reactor module (*Fischer Manual,* 1985). The pulsing control unit has an input capacity of 1.0 kW and an impulse capacity of 4.0 kW. The pyrolysis time and the reactor base temperature could be preselected. The solenoid valve directed the flow of carrier gas either directly to the gas chromatograph or via the pyrolysis chamber to the gas chromatograph injection port, Figure 2.

The schematic diagram of the microreactor is shown in Figure 3. The reactants were encapsulated in a glass microreactor

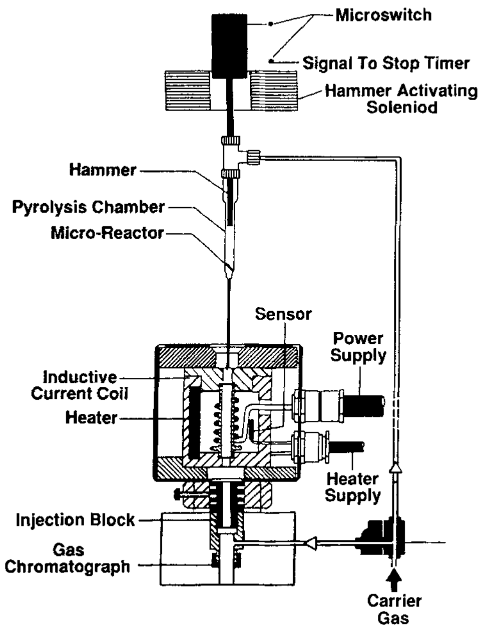

Figure 2. Curie Point pyrolyzer with microreactor and quench system.

to ensure that the pyrolysis products did not escape the reaction zone. It is to be noted that the reaction zone between the ferromagnetic heating element and the walls of the microreactor is 55 μm. This distance was kept to a minimum intentionally to ensure that the reactants had the same temperature profile as that of the ferromagnetic heating element.

The TRT profiles for final temperatures of 700, 800 and 900°C were measured by 25-μm thermocouples spotwelded onto the ferromagnetic wires. The TRT's were measured to be 46, 65 and 84 ms for the three temperatures, respectively, from an ambient temperature of 300°C (Rastogi, 1987). To keep the TRTs to a minimum, the pyrolysis was carried out with one wire per microreactor (ampoule).

During the pyrolysis process, the carrier gas was routed to flow through the pyrolysis chamber. The quench system consisted of a hammer which was activated by a solenoid. In turn, the solenoid was activated by a timer control unit. A solenoid operated hammer broke the vial at the required residence time so that the products could be quenched and swept directly by the carrier gas into the GC column for analysis.

Since the reaction times are in milliseconds, it was realized that the dynamics of the microreactor system were very important. The time it takes for all the key operations, i.e., activating the solenoid system, response time of the microswitch, and the time of travel of the hammer, all take a finite time that could not be neglected. It was also realized that these response times were not constant and could not be controlled. Therefore, a delay timer-control unit was designed that would take these response times into account every time the system was used, and would measure and display the actual residence time of the reaction.

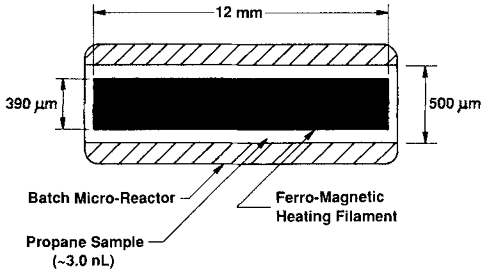

Figure 3. Microreactor with enclosed ferromagnetic wire and propane gas sample.

The operation of the delay timer control unit is shown in Figure 4. The timer control unit consisted of a start switch, two delay timers, A and B, and a display counter with a reset switch. Delay timers A and B were activated with the start switch. Delay timer B activated the display counter timer and the Curie Point pyrolyser. Delay timer B was set at the average time taken by the system to respond. Delay timer A activated the solenoid which, in turn, activated the microswitch. Delay timer A was set to the required pyrolysis time. The microswitch, shown in Figure 2, was movable and was adjusted so that it was activated by the solenoid at the instant the hammer broke the vial. The microswitch stopped the display counter timer and started the gas chromatograph. Hence, after the pyrolysis reaction, the display on the timer gave the actual pyrolysis time of the reactants. It is to be noted that the counter timer and the pyrolyzer were activated simultaneously, and the counter timer was stopped when the vial was broken. Hence, the display counter timer recorded the actual pyrolysis time rather than the set pyrolysis time, thereby taking into account the dynamics of the system. The reaction time could be controlled by this apparatus and had the accuracy to within 1 ms.

To verify that the sample and its surroundings were at the same temperature, a simplified computer simulation of the unsteady state heat transfer within the microreactor for the worst case scenario (i.e., heat transfer by conduction only; no radiative or convective effects) was performed (Rastogi et al., 1987). This simulation indicated that, even under such a worst case scenario, confined microgram quantities of gaseous hydrocarbon samples would reach the temperature of the ferromagnetic wire within one degree in less than 0.2 ms. Hence, the temperature rise time (TRT) of the microreactor would be the same as the measured TRT of the ferromagnetic heating wire (Rastogi et al., 1987).

Although short TRT's and reproducible equilibrium temperatures may be easily obtained, the decrease in filament temperature after shutting off the power is slow in comparison to the initial TRT. The reaction products will be quenched much faster, since direct gas mixing results in very fast quenching, with the cooling rates in excess of 10^6 K/s (Sundstrom and DeMi-

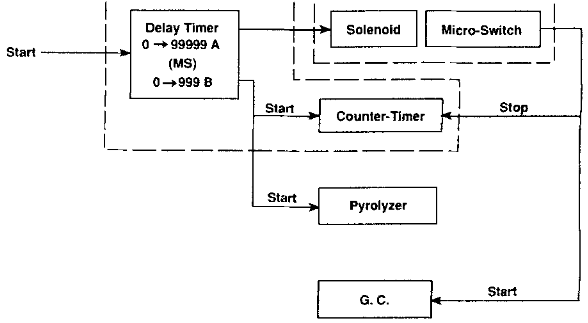

Figure 4. Pyrolyzer-delay timer setup.

chiell, 1971). The Reynolds number calculated for this mixing was greater than 3,000, showing that the flow was turbulent and high rates of heat transfer would occur. Therefore, it is expected that the reaction products will be quenched in less than 1 ms. Hence, the microreactor system allowed careful control and establishment of the temperature profiles experienced by the reactants.

The analysis system consisted of a Varian 6000 gas chromatograph, Varian CDS 401 control station, Apple IIe microcomputer and a Varian printer. The start switch sequentially activated the process, whereby pyrolysis reactions took place, the solenoid-operated hammer shattered the vial, and the quenched products were swept directly to the gas chromatograph for analysis. The entire process was fully automated.

Experimental Results and Discussion

The experimental results that are presented in this section are related to the products formed from the pyrolysis of propane. The main independent experimental variables were temperature and the pyrolysis time, whereas the experimentally determined variables were the percent conversion of propane and the composition of the products formed.

Nanoliters of propane, carefully enclosed in the microreactor, were pyrolyzed at four different temperature levels: 600, 700, 800 and 900°C. The pyrolysis times were varied from 0 to 2 s for 600–800°C and from 0 to 1 s for 900°C. The pyrolysis time included the TRT and the equilibrium temperature time.

For comparison purposes, three computer simulations were performed assuming a constant volume mixed batch reactor. It should be noted that the temperature rise times were included in the simulations. In the first simulation, the molecular scheme of Sundaram and Froment (1979) was used. The product distribution involved 11 components. Another simulation was performed using the radical reaction scheme proposed by Layokun and Slater (1979). The simulation involved the mass balances of seven molecular species and four radical species. A simple reaction scheme presented by Kershenbaum and Martin (1967) to predict the kinetics of nonisothermal pyrolysis of propane was also used. The simulation involved the primary decomposition reactions yielding the primary products. In the three simulations, pseudosteady-state approximation was not used. Relaxation of the pseudosteady-state assumption altered the results of the model predictions.

The variation of conversion with reaction times for four different temperatures are shown in Figures 5–8. The data of other workers have been shown for comparison purposes. Figure 5 shows the conversion of propane at 600°C for residence times up to 2,200 ms. It can be seen that the experimental data values are about 5–8% higher than those predicted by simulations of Froment et al. (1979) and Kershenbaum and Martin (1967) or the results obtained by Layokun and Slater (1979). Since tubular reactors were used in these studies, the temperatures presented in the literature are probably suspect. The figure does show a definite trend; increasing conversion with increasing reaction time.

Figure 6 shows the conversion of propane at 700°C. The data of Layokun and Slater (1979) matches the obtained experimental data quite closely. However, their reaction simulation predicts a higher conversion. The conversion predicted by the reaction schemes of other workers is lower than that obtained in this work.

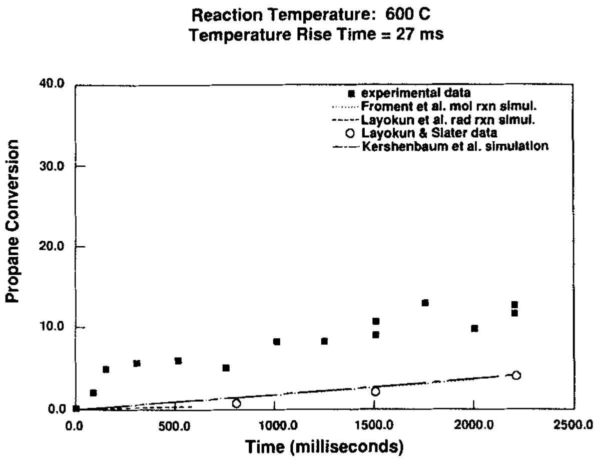

Figure 5. Variation of conversion with reaction time at 600°C.

Figure 7 shows that at 800°C, the data of Herriott et al. (1972) closely matches the experimental data of this study over the entire range. The data and the prediction by reaction schemes of other workers are slightly higher than the experimental data. Trimm and Turner's (1981) data at 810°C shows a lower conversion than other workers used in this comparison.

Inhibition effects become evident at higher temperatures. Inhibitors reduce the concentration of reactive free radicals in a reaction thus lowering the rate of reaction to some finite, nonzero level. There are two kinds of free radical inhibitors: a) those which react with the existing free radicals to yield nonreactive stable molecules (e.g., nitric oxide) and b) those which form free radicals themselves, which are not as efficient chain carriers as were the original free radicals (e.g., propylene). In the case of propane pyrolysis reaction, the products formed fall under the second category.

As seen from Figure 8 there is a lack of experimental data for 900°C. The reaction simulations however predict a much faster reaction than that shown by the experimental data. This could be due to the problems associated with extrapolating their reaction schemes to a higher temperature. Since these reaction schemes were developed from experimental data taken at lower

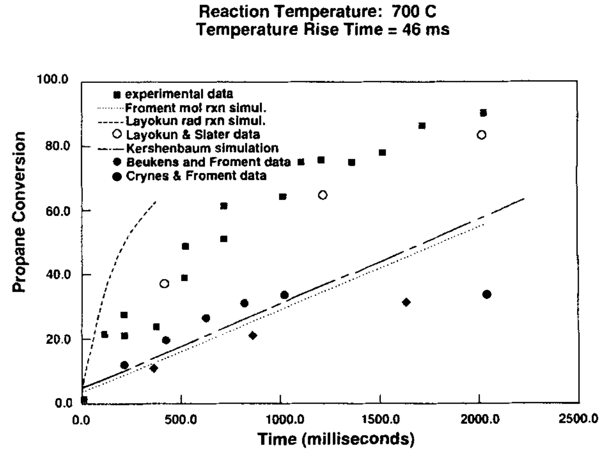

Figure 6. Variation of conversion with reaction time at 700°C.

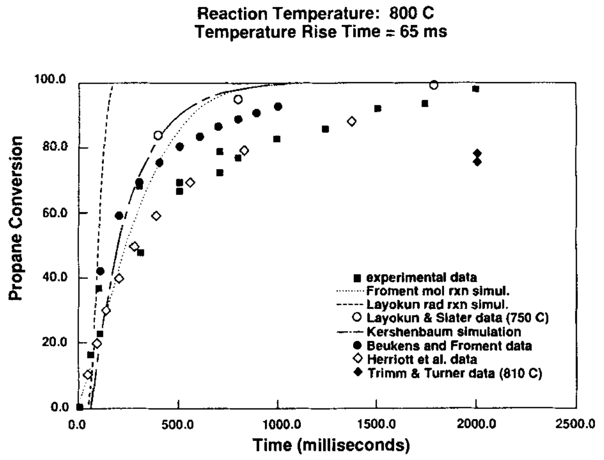

Figure 7. Variation of conversion with reaction time at 800°C.

temperatures, where inhibition effects are insignificant, it is probable that these effects were not taken into account when developing these reaction schemes. Therefore, it is not surprising that these reaction schemes are not particularly applicable at higher temperatures. By not taking inhibition effects into account could explain the reason that the simulation results of other workers are higher than the experimental values at 800 and 900°C.

The lower conversions at higher temperatures could also be due to the effect of rapid quench in the experimental setup of this work. Since other workers have not used direct quench techniques, the reaction would continue in their quench section especially at higher temperatures, resulting in higher conversions.

A number of preliminary experiments were done to determine the primary products resulting from the thermal decomposition of propane. The results from the experiments show that the primary products are methane, ethylene, hydrogen, and propylene. The pyrolysis reaction is not as fast as predicted by the models of the other workers and the experimental yield of methane is lower. By using better quench techniques, the experimental yield of olefins was higher than that of other workers.

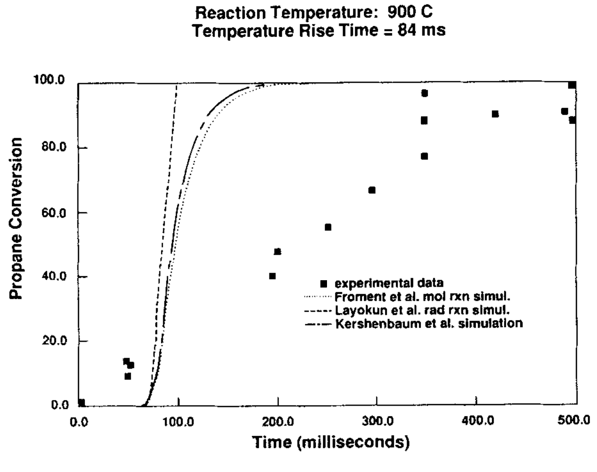

Figure 8. Variation of conversion with reaction time at 900°C.

Based upon the postulation of first order kinetics, the kinetic parameters for the overall decomposition of propane were determined. The half lives of the reaction were calculated from the evaluated rate constants at four different temperatures and are tabulated below:

Temp.	$t_{0.5}$ (ms)
600°C	14,270
700°C	663
800°C	422
900°C	88

This shows that the reaction is slow at 600°C and becomes fast at 900°C.

In comparing the results of propane decomposition by other workers, it is important to realize that most other research has been done at much lower temperatures. Figure 9 compares most of the published data for first order propane pyrolysis. A value of 136 kJ/mol was calculated for the activation energy. All other studies have noted higher activation energies, usually between 210 and 290 kJ/mol.

The reason for this can be explained by the difference in temperature at which the studies were conducted. Several previous workers (Laidler et al., 1962; Martin et al., 1964; Kershenbaum, 1964) have noted that as the temperature of the hydrocarbon pyrolysis is increased, the activation energy for the reaction "appears" to decrease rather than remain constant. This effect can also be noted in this work. This effect is explained by the inhibition effect which causes the reaction rate at higher temperatures to be somewhat lower than that predicted by the Arrhenius expression. If it were simply a decrease in the activation energy, the rate at higher temperatures, would increase rather than show a decrease. Thus, while such an effect has been termed as "an apparent decrease in activation energy," it is important to realize that the true cause of this phenomenon is mechanistic. Hence it should be stated that there is *no* evidence for a temperature dependence of the activation energy.

The reactant in this work was pure propane without any inerts and unlike other workers the conversion was not kept purposely to a minimum. Also, since the products and the reactant were enclosed, inhibition effects for the experiments conducted in this study would tend to be higher than that observed by other workers. Olefins in general and propylene, in particular, are strong inhibitors of free radical reactions (Kershenbaum, 1964). Their presence inhibits the conversion of the reactant. As the reaction

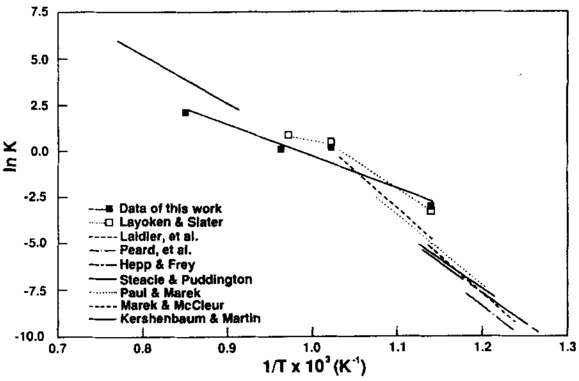

Figure 9. Comparison of activation energy.

temperature is increased, the mole fraction of propylene and other olefins increases, which results in a larger inhibition effect causing the result shown in Figure 9.

Kinetic analysis was performed on the experimental data between temperatures of 600 and 700°C and yielded an activation energy of 216 kJ/mol which is closer to the range of other workers. It should be noted that the conversions even at these lower temperatures are much higher than those of the other workers. However, as seen from Figure 9, the results of this work at these temperatures match very closely the data of Layokun and Slater (1979).

The basic mechanism of the propane pyrolysis reaction remains the same. A model using 87 free radical equations has been used to predict the conversion and product distribution for the pyrolysis of propane (Rastogi, 1987). High inhibition of the reaction gave lower values of the apparent activation energy when calculated over the entire temperature range. But the values of activation energy approached those found in the literature when conversions were lower. Temperature control and the actual reaction time are the key variables which control the reaction.

Conclusions

The measurement of kinetics of hydrocarbon pyrolysis especially at higher temperatures requires the careful establishment of the temperature profile experienced by the reactants. Temperature-rise times and quench times which have been neglected by previous workers, are important variables which have a significant effect on the reaction conversion and product distribution. Though the reaction mechanism remains the same, interlaboratory irreproducibility in the measured conversion and product distributions has led to the proposal of significantly different reaction schemes.

The reactor systems used by other workers were found to be inadequate for the precise study of kinetics of hydrocarbon pyrolysis reactions. A microreactor system has been developed to study fast pyrolysis reactions, which involve millisecond reaction times. This novel reactor system uses direct gas quench to ensure a rapid freezing of the reaction. This apparatus has the capability to generate precise data at low conversions which can be used to analyze the reaction at its initial rate and determine its reaction kinetics.

The propane pyrolysis reaction has been studied at temperatures of 600, 700, 800 and 900°C. The pyrolysis reaction is not as fast as predicted by the models of other workers. The present experiments yielded a lower mole percent of methane and a higher mole percent of useful olefins. Analysis of the data at low conversions yielded an activation energy of 216 kJ/mol which is in the range of other workers. Precise data with known experimental conditions can be generated easily with the novel microreactor/gas chromatograph system.

Acknowledgment

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