ULTRAPYROLYSIS OF HEAVY OILS: REACTION KINETICS AND REACTOR TECHNOLOGY

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ABSTRACT. This contribution covers recent progress on heavy oil pyrolysis considering the following topics: reaction mechanisms, pyrolysis of mixtures, and reactors for kinetic studies. Furthermore, a review concerning ongoing studies on the kinetics of heavy oil ultrapyrolysis/upgrading along with a description of the new generation reactors under development at the University of Calgary, Alberta is also presented.

1. Introduction

Pyrolysis, thermal pyrolysis, thermolysis, thermal cracking, non-catalytic cracking, and gasification are all terms which refer to approximately the same generic reaction: the scission and recombination of molecules due solely to the provision of sufficient thermal energy to allow the reactions to proceed, in the absence of oxygen.

The pyrolysis of hydrocarbons in general and light hydrocarbons in particular has long been a reaction of commercial importance. For years, pyrolysis has been implemented in refineries as a primary method for producing gasoline from heavier petroleum fractions. More important, though, is the application of hydrocarbon pyrolysis for the production of olefins, the basic feedstock for the petrochemical industry. Economically, this is one of the most important reactions used industrially since the mid-1950's. Various feedstocks have been employed to meet the olefin demand in the world. In Canada and United States most olefin production plants are usually ethane- or propane-based, in view of the abundant natural gas reserves. In contrast, Europe and Japan have traditionally relied on naphtha as a feedstock. However, because of the predicted limited future supply of light feedstocks, producers have begun to shift to heavier feedstocks (gas oil, residual oil and even the whole crude itself).

In Canada, a significant interest exists in the development of new and efficient, economical and reliable methods of exploiting the remaining energy resources. In particular, because of the vast existing resources in the form of heavy, or high molecular weight, hydrocarbons (so-called heavy oils or tar sands bitumens), there is an urgent need to develop efficient means of upgrading these to lower molecular weight feedstocks, which can be handled and utilized in the manner of the lighter, conventional hydrocarbons. Present methods used industrially for upgrading heavy oils include fluid coking and delayed coking. These technologies reject typically 17 and 25 percent of the feedstock as coke and other non-usable byproducts, respectively (Schumacher, 1982). At present, large amounts of coke are stockpiled because of potential hazards to the environment (sulphur and heavy metals content) in economically disposing of them with current technology. Thermal cracking of heavy hydrocarbons, under specific operating conditions, may constitute an efficient and economical upgrading method.
1.1. CLASSIFICATION OF PYROLYSIS PROCESSES

Bergougou and co-workers (Mok et al., 1984; Graham et al., 1986; Berg et al., 1986) have developed, in the course of their work on the pyrolysis of wood, cellulose and hydrocarbons, a terminology to deal with the increasing severity of the thermolytic pyrolysis processes. Slow pyrolysis is defined as a process which takes place at temperatures less than 500°C, in which the feedstock is heated at low rates (< 2°C/s), and in which the reactant resident times are measured in the scale of minutes to hours.

Flash pyrolysis is defined as that set of processes in which the heating rate is greater than 2°C/s, for which the maximum temperature is in the range of 400 to 600°C, and the residence times of the vapour reagents and products range up to 2 s.

Fast pyrolytic processes incorporate heating rates of 200 to 1000°C/s, temperatures higher than 600°C, and short vapour residence times (< 0.5 s).

Ultrarapid pyrolysis, or ultrapyrolysis, constitutes that class of processes capable of heating rates greater than 1000°C/s, with residence times between 10 and 800 ms, and conducted at temperatures up to 1000°C. In general, what differentiates processes operating under each of the above categories is the resulting product spectrum. The slower, less severe processes yield a relatively greater proportion of undesirable byproducts (e.g. coke). Figure 1 illustrates a generic pyrolytic reaction pathway, including the speed of the reactions involved. On the basis of the above classification, it can be expected that fast pyrolysis processes, and in particular ultrapyrolysis, can take advantage of the differences in the rates of the competing reactions to maximize the yield of desirable light products.

1.2. HEAVY OIL PYROLYSIS MECHANISMS

The thermal pyrolysis of hydrocarbons in general can be characterized as a set of fragmentation and recombination reactions which occur in series and parallel. Any given reaction, in accordance with the generally accepted free-radical chain mechanism produces either final product or feedstock for further reaction.