CHAPTER I

INTRODUCTION

In 1973, the uncertainty and expense of crude oil caused by the Arab oil embargo made the rest of the world aware of the importance of developing long-term, viable, alternative fuel sources. This awareness was later extended to a general realization of just how finite are the supplies of all our resources and prompted a global resource conservation movement. Vigorous investigations followed in all the energy fields, except nuclear, concentrating on synthetic fuels from coal, oil shale, tar sands, heavy oil, peat and biomass, and energy from solar and geothermal sources [176]. Most research work in the United States was coal-oriented mainly due to its abundance and its almost mature technology derived through long historical progress [67,90]. The development of biomass-derived fuels also took a sharp upward turn, not only because of the capability to generate less pollution, but also because of the accessibility to a wide variety of renewable feedstocks [136,137,202,239]. In recent years, however, the recession overshadowed and slowed down energy research, demonstrating progress in this area will be greatly influenced by economic and political factors.

A project funded by the U.S. Government since 1975 was undertaken in the chemical engineering laboratory at Arizona State University to investigate a conversion process which transforms biomass materials into transportation grade liquid hydrocarbon fuels and/or alternative high value chemical products via a thermochemical indirect liquefaction process [138]. The basic conversion scheme is depicted in Figure 1.1 in which the biomass is first thermally decomposed into mainly gaseous components [136,186]. The gasification system consists of a dual fluidized bed unit with solids circulating between a pyrolyzer and a generator [118]. The pyrolyzer is operated in a "fast" pyrolysis mode [103,184] to minimize char and tar formation [122,194,196]. The gaseous products from the gasification unit mainly are carbon monoxide, methane, hydrogen, ethylene and carbon dioxide in the proportions shown in Table 1.1 [136].

Initial study of the downstream modified Fischer-Tropsch synthesis for the project was made by Fleming [87]. The liquid product from the synthesis reactor is composed of two immiscible phases [87]. The lighter water-insoluble organic phase consists primarily of paraffinic hydrocarbons in the C_7-C_{30} range and is free of oxygenated compounds [171]. This product is most similar to JP-4 jet fuel in structure [137,227]. High

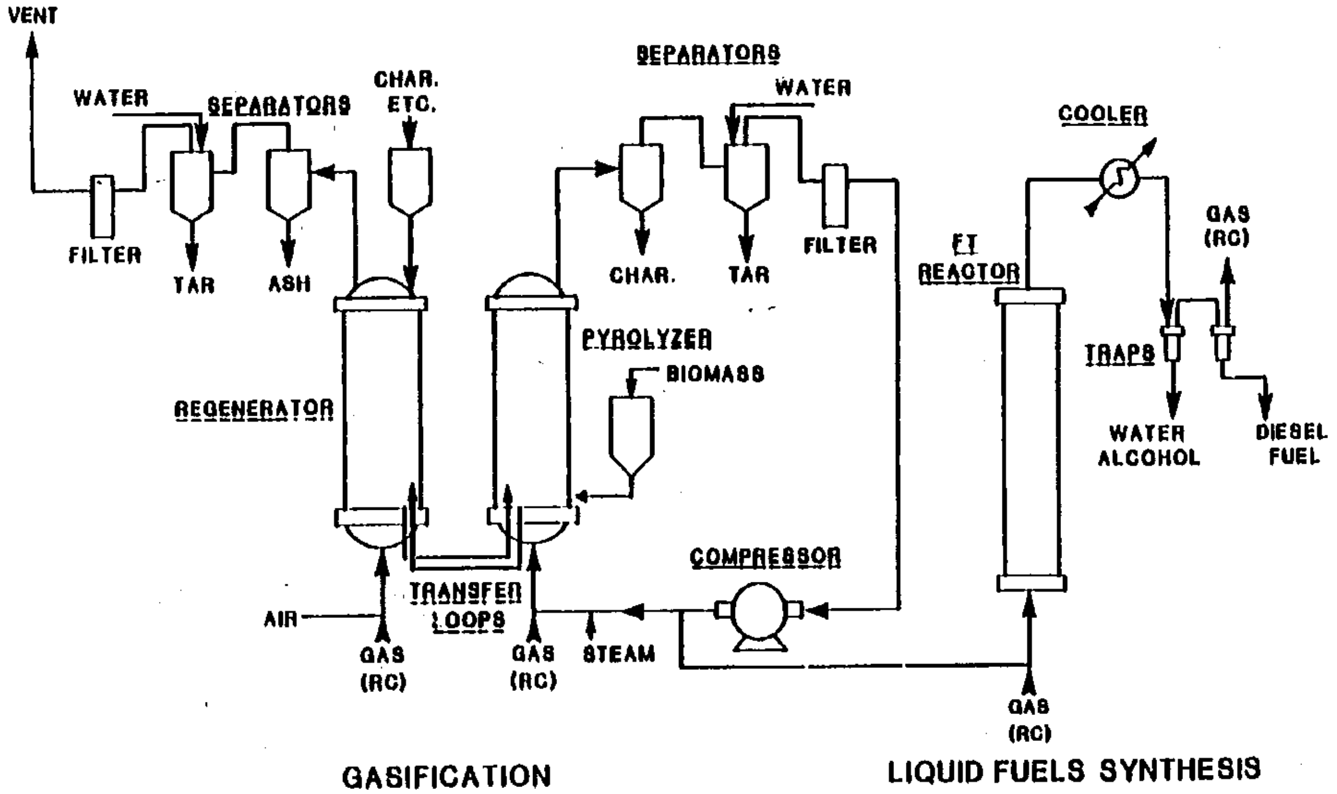

Figure 1.1. ASU Biomass Conversion Process - Schematic.

Table 1.1. Composition of Biomass Derived Pyrolysis Gas.

Component	Mole Fraction
Hydrogen	0.10 - 0.45
Carbon monoxide	0.15 - 0.60
Ethylene	0.05 - 0.40
Carbon dioxide	0.00 - 0.15
Methane	0.10 - 0.45
Ethane	0.01 - 0.05

octane fuel was obtained by further reforming this organic product in a fixed-bed reformer using a conventional reforming catalyst [56,102]. A simple distillation of the paraffinic organic product will produce a fuel in the range of No. 2 diesel [137]. The heavier aqueous phase product consists primarily of normal propanol and water [87,171]. The synthesis gas reaction system has been operated in both fluidized bed and slurry phase reactors [45,87,227,249]. A new study is also underway for producing more valuable speciality chemicals from the synthesis gas mixture using shape-selective zeolites blended with Fischer-Tropsch type catalyst ingredients [138].

Integration of upstream gasification and downstream liquefaction systems together in a continuous operation mode has been achieved [138]. At present, while bench scale study of the project continues and the project may soon enter its third phase of operation, i.e., pilot plant production [138], little work has been done in the past on the study of the kinetics of the downstream modified Fischer-Tropsch synthesis [121]. This is because the main emphasis of the project was to demonstrate the capability of producing high yields of quality liquid hydrocarbon fuel by the process. With this goal being achieved, the need for a better understanding of the nature of the synthesis process and its relation to the catalyst has risen. A reliable kinetic model, i.e., rate equation, that not only can supply such information, namely, can adequately explain the conversion and selectivity data from laboratory reactor experiments, but also can provide guidance for optimally operating pilot reactors, is therefore highly desirable. A successful commercial reactor design also relies heavily on the accuracy of the kinetic model.

For a complex, heterogeneous reacting system, where large number of chemical species are transferred between phases (fluid and solid) and participate in numerous simultaneous reactions, the identification and separation of each individual species can be very difficult and costly even with today's most sophisticated analytical instruments. Totally empirical correlations sometimes are utilized, but often suffered from the problem of inadequate extrapolation beyond the range of the data from which they were obtained [233]. "Lumped kinetics" is sometimes employed to establish semi-empirical models [232]. Still another more theoretical approach is to formulate the rate equations based on the assumed mechanism of adsorption phenomena and the concept of active sites [116].

As the reactors are scaled up to their integral sizes where higher rates of reaction are desired, significant coupling of chemical reactions with physical transport phenomena will definitely make it more difficult to separate the effects. Therefore, most kinetic experiments are normally carried out in differential reactors where the conversion is kept low (only a few percent) and the physical transport effects are minimized [46,72,156,231], so that the intrinsic behavior of the surface reaction can be directly observed.

It is the objective of this research to obtain such a theoretical kinetic model derived from a proposed mechanism using Hougen and Watson's method [117] for the modified Fischer-Tropsch reactions (MFTR), i.e., incorporation of ethylene in the classical Fischer-Tropsch synthesis (FTS). A tubular fixed-bed microreactor held at nearly constant temperature in a fluidized sand bath will be employed for the experiments. A cobalt based catalyst was selected for this study as determined by prior yield and stability investigations [45,87,227]. The cobalt catalyst supported on ALCOA activated alumina by an impregnation technique will be ground and screened to a finite range of particle sizes and will be characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and conventional volumetric chemical adsorption. The regime where intrinsic surface reaction controls is to be first experimentally determined from a temperature study. Verification of negligible resistances to both external and internal diffusion gradients will be done by examining the reaction rates with varying mass velocity of feed, while maintaining the same space velocity, for three different particle sizes of same catalyst at different reaction temperatures. Theoretical calculations of the gradients will also be performed to check the validity of the insignificance of internal gradients.

Once the justification of experimental conditions has been established, kinetic experiments can be executed in a straightforward manner by varying the feed compositions over a reasonable range. On-line gas chromatography will be employed to monitor the net conversion of active reactant species, namely hydrogen, carbon monoxide and ethylene, to ensure that the differential condition is not violated. The basic data to be obtained will consist of the reaction rate versus reaction temperature and partial pressures of six dominant components, i.e., hydrogen, carbon monoxide, ethylene, carbon dioxide, methane and ethane, at steady state. A nonlinear regression routine (Marquardt method) [151] will be used to determine the values of the kinetic parameters. Model assessment will be performed via statistical analysis and physical compatibility from the experimental data. The study plan is illustrated in Figure 1.2.

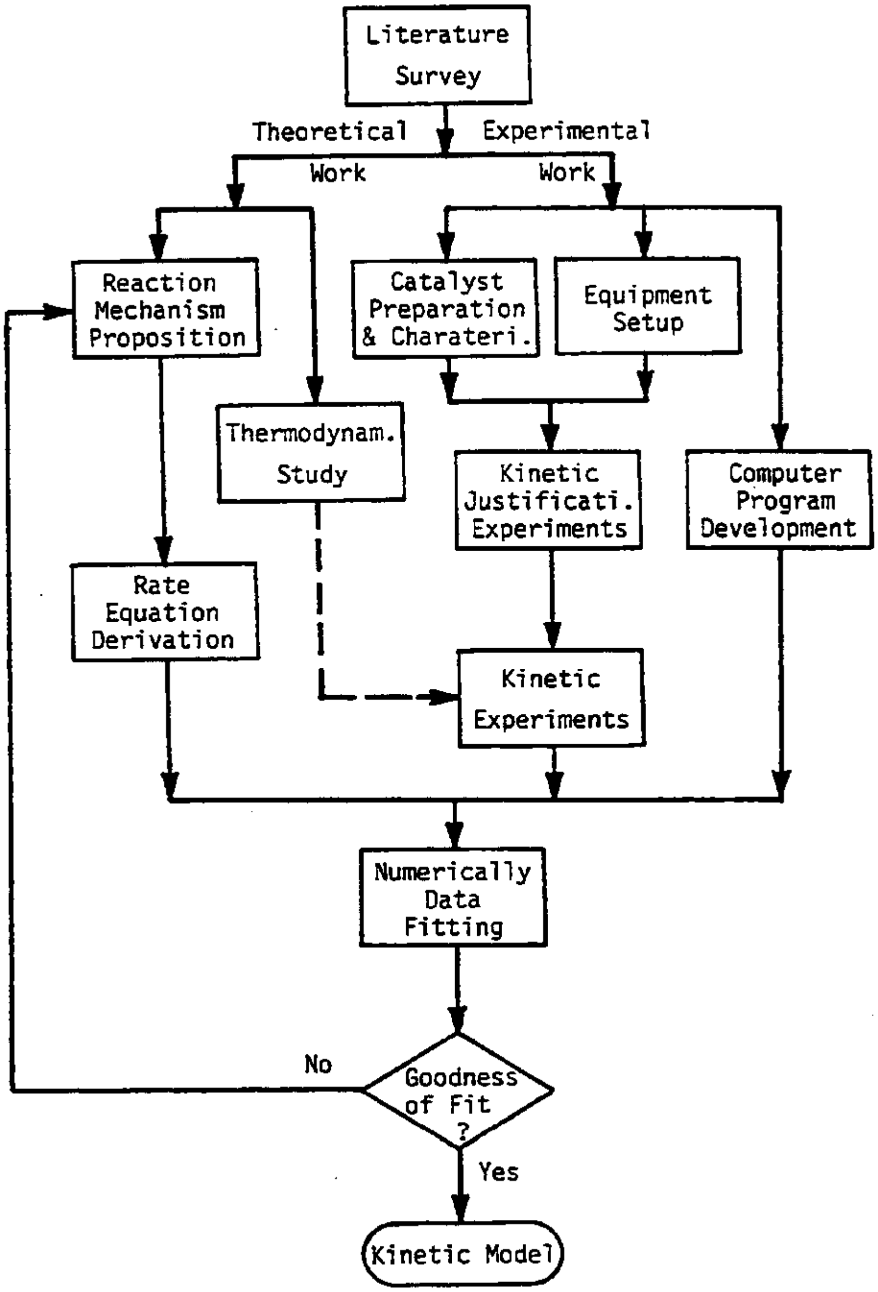

Figure 1.2. Study Plan.