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THE ECONOMICAL PRODUCTION OF ALCOHOL FUELS FROM COAL-DERIVED SYNTHESIS GAS

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TABLE OF CONTENTS

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LIST OF TABLES

LIST OF FIGURES

Executive Summary

During this reporting period in Task 1, at WVU, we continued with the three major thrusts of the program. We completed our preliminary studies on the use of a membrane reactor for a BASF methanol synthesis catalyst, and the results were compared qualitatively with those from a non-permeable stainless-steel tubular reactor. Consequently, we re-started our screening of promising non-sulfide Mo-based catalysts and more detailed parametric studies on selected non-sulfide catalysts. Secondly, we continued the kinetic study of a sulfided carbon-supported potassium-doped molybdenum-cobalt catalyst in the Rotoberty reactor. We also finished our post analyses of previous promising screening runs of non-sulfide molybdenum-based catalysts by analyzing the liquid products collected using a GC/MS.

At UCC, we tested the effect of high-temperature heat treatments of selected catalysts. In all cases, heat treatments resulted in decreased total alcohol selectivity and decreased space time yield to all products affected. During this quarter, we have completed catalyst screening at UCC. We have simultaneously met three of four catalyst development targets. Oxygenate selectivity has been our main hurdle. No catalyst scale-up testing is planned. We do plan to complete characterization of selected catalysts.

During the past three months in Task 2, the following has been accomplished in fuel testing. Three blends have been selected for future runs. We have completed an analysis of sampled in-cylinder pressure traces to determine knock limits. Adjustment of the sampling system to increase accuracy of the collected exhaust samples has been completed. Electric wiring has been modified to suppress noise in different sensor's output signal. A comparison of measured to calculated fuel to air ratio has been done.

The program which will optimize the alcohol fuels blending facility has been improved. The primary focus was on calculating the manufacturing cost of the synthesis gas used to make the alcohols, and making certain that the algorithm is ready when Task 1 results are available.

1.1 Introduction

The objective of Task 1 is to prepare and evaluate catalysts and to develop efficient reactor systems for the selective conversion of hydrogen-lean synthesis gas to alcohol fuel extenders and octane enhancers.

Task 1 is subdivided into three separate subtasks: laboratory and equipment setup; catalysis research; and reaction engineering and modeling. Research at West Virginia University (WVU) is focused on molybdenum-based catalysts for higher alcohol synthesis (HAS). Parallel research carried out at Union Carbide Corporation (UCC) is focused on transition-metal-oxide catalysts.

1.2 Accomplishments, Results and Discussion

1.2.1 Laboratory Setup

During this reporting period, we completed our preliminary studies on the use of a membrane reactor for a BASF methanol synthesis catalyst. As a result, we re-converted the reactor to a conventional plug-flow reactor, which allows us to screen more of the promising non-sulfide Mo-based catalysts and to carry out detailed parametric studies on selected non-sulfide catalysts. However, we experienced both hardware and software problems with the computer used to control the reactor system and gas chromatograph. The computer was finally replaced, and the problems were solved, at least temporarily. We are continuing our studies on non-sulfide Mo-based catalysts in this reactor system.

In the Rotoberty reactor setup, we successfully modified the reactor to study the effect of trace amounts of alcohols in the feed stream. This was achieved by pumping the liquid into the reactor from the top using an HPLC pump. Nevertheless, this system developed a problem with the motor controller which, along with the stator assembly, was shipped back to the manufacturer for repair. Therefore, this system was idle for more than one month.

1.2.2 Molybdenum-Based Catalyst Research

At WVU, we continued our kinetic study of a sulfided carbon-supported K-doped Mo-Co catalyst in the Rotoberty reactor. Detailed results can be found in MS53 and MS54. The study is not yet complete, due to a failure of feed gas delivery and a problem with the motor controller.

Preliminary experimental investigations on the use of a membrane reactor for a BASF methanol synthesis catalyst have been completed. Detailed results and a qualitative comparison with results from a non-permeable packed-bed tubular reactor can be found in MS52 and MS53. We are still carrying out a more-detailed quantitative analysis.

We also finished our post analyses of previous promising screening runs of non-sulfide Mo-based catalysts. The results were presented in MS54.

1.2.3 Transition-Metal-Oxide Catalyst Research

At UCC, we tested the effect of high-temperature heat treatments of selected catalysts. Two different heat treatment processes were applied to a few of our more promising catalysts. These two processes differed mainly in the duration at elevated temperatures and the cool-down rate. Copper-containing catalysts (0.18 pph Cu and 5 pph Cs on an Engelhard Zn / Cr support) were run first. Heat treatments lowered the selectivity to total alcohols and space time yields to all products. Although the copper loading was very low, we thought it possible that the effect was due to copper sintering. We then tested a catalyst containing 5 pph Cs and no copper, but the effect was the same.

1.3 Conclusions and Recommendations

Reduced Mo-Ni-K/C materials are promising catalysts for HAS. Large amounts of alcohols were generally produced for optimized catalysts. However, the product distribution is very much more complicated, compared to that from sulfided catalysts. Heat treatments of transition-metal catalysts decrease total alcohol selectivity and space-time yield for all products.

1.4 Future Plans

At WVU, work will resume on the screening of promising non-sulfide Mo-based catalysts and on the more-detailed parametric studies on selected non-sulfide catalysts using the plug-flow reactor. The kinetic study using the Rotoberty reactor will continue.

UCC has completed catalyst screening. We have simultaneously met or exceeded three of four catalyst development targets with our best catalyst. No catalyst simultaneously met all four catalyst targets: 1) total alcohol selectivity $> 90\%$; 2) total alcohol space time yield $>$ 320 g/kg catalyst/hour; 3) carbon monoxide conversion > 20 percent; and 4) molar methanol composition of total alcohol product $< 70\%$. Oxygenate selectivity was our main hurdle. No catalyst scale-up testing is planned. We do plan to complete characterization of selected catalysts.

2.1 Introduction

In fuel testing, efforts have focused on selecting blends for future runs and calibrating equipment. Knock limits have been studied. The sampling system has been adjusted to improve accuracy. Electrical wiring has been modified to suppress noise.

During the past quarter, we have worked on improving the program which will optimize the alcohol fuels blending facility. The primary focus was on calculating the manufacturing cost of the synthesis gas used to make the alcohols, and making certain that the algorithm is ready when Task 1 results are available.

2.2 Accomplishments, Results, and Discussion

2.2.1 Fuel Testing

Several adjustments and modifications to the current system have been done. These are detailed below.

Three blends have been selected for future runs. Restricting the alcohol blends to contain ≤ 3.7% oxygen by weight and amount of total alcohol to 10% by volume, the following blends are considered:

Lower Limiting Blends
with C_2 fixed at its lower limit of 2.4%, C_4 and C_5 varying between 0.0% and 1.6%, and C_1 and C_3 are calculated such that total alcohol=10% and oxygen = 3.7% by weight. C_1 varies between 3.02% and 3.26% while C3 varies between 2.74% and 2.98%.

Midrange Blends
with C_1 and C_2 fixed at 2.0%, C_3 fixed at 3.0%, and C_4 and C_5 varying between 0.0% and 3.0%, all blends are below 3.7% oxygen by weight.

Upper Limiting Blends
with C_1 fixed at its lower limit 0.6%, C_3 fixed at its upper limit of 4.8%, C_4 fixed at its upper limit of 2.5%, and C_2 and C_5 varying between 0.0% and 2.2%, all blends are below 3.7% oxygen by weight.

An analysis of sampled in-cylinder pressure traces to determine the knock limit has been performed. Figures 2.1 and 2.2 show the sampled in-cylinder pressure trace for a knocking and non-knocking cycle. The odd derivatives of the pressure trace are used to identify whether the engine is knocking or not.

The sampling system has been adjusted. In the previously conducted runs using alcohol blends (10% by vol.), low concentrations of unburned alcohol and aldehydes are obtained in the exhaust sample. In order to increase the capability of the sampling system to measure these low concentrations accurately, the dilution factor (dilution air to exhaust sample) is lowered by adjusting the mass flow controllers. Also, the volume of distilled water in the bubbler (used to capture unburned alcohol) is to lowered from 25 mL to 10 mL for future runs.

Electric wiring has been modified to suppress noise in different sensor's output signal. At the time of spark, an overshoot in the in-cylinder pressure trace is observed. This is due to the large noise generated by the spark signal. In order to minimize this effect, a new low-noise spark plug cable is installed. Also, the wiring arrangement is re-checked and necessary changes are made.

The measured to calculated fuel to air ratio has been compared. The measured air to fuel ratio is obtained from measurements of mass flow rates of induction air and fuel. Another method of calculating air to fuel ratio is from measured concentrations in the exhaust gas sample. Employing a simplified combustion reaction for a general fuel $C_{\alpha}H_{\beta}O_{\gamma}N_{\delta}$, the equivalence ratio, ϕ, is given by:

$$\phi=\left[\frac{\frac{2}{3}(kDCO_2+DCO)+\frac{28.97}{18.02}\omega DCO}{k\Gamma DCO_2-\Omega DCO}\right]\cdot\left[\frac{\alpha+0.25\beta-0.5\gamma}{0.21}\right]$$

where

k is the reaction constant for $CO_2+H_2 \leftrightarrow CO+H_2O$,
DCO_2 is the dry concentration of CO_2 in the exhaust sample,
DCO is the dry concentration of CO in the exhaust sample, and
ω is the humidity ratio in the induction air.

Γ is given by:

$$\Gamma=\frac{-\alpha}{6X}((z+4)DHC-4+2DCO)-\frac{1}{3}\left(\gamma-\frac{\beta}{2}+\delta\right).$$

Ω is given by:

$$\Omega=\frac{-\alpha}{3X}((z-2)DHC+2-DCO)+\frac{1}{3}(\gamma+\beta+\delta).$$

X is given by:

$$X=DCO_2+DCO+DHC.$$

DHC is the concentration of hydrocarbons in the exhaust sample and z is the hydrogen to carbon ratio in the measured concentration.

Table 2.1 shows a good agreement between the calculated and the measured equivalence ratios for different tests.

Table 2.1 Measured versus calculated equivalence ratio

Num.	Sample ID.	Equivalence ratio		Relative Error (%)
		measured	calculated	
1	1121B10.BSE	0.74	0.73	2.43
2	1121B01.BSE	0.86	0.82	4.54
3	1121B02.BSE	0.87	0.82	5.32
4	1121B03.BSE	0.88	0.83	5.34
5	1121B04.BSE	0.95	0.91	4.50
6	1121B05.BSE	1.02	0.96	6.15
7	1121B06.BSE	1.07	1.01	6.21
8	1121B07.BSE	1.15	1.10	4.72
9	1121B08.BSE	1.24	1.20	3.72
10	1121B09.BSE	1.29	1.25	3.34
11	1129B11.BSE	0.72	0.71	1.37
12	1129B08.BSE	0.86	0.82	4.76
13	1129B05.BSE	1.02	0.96	5.12
14	1129B01.BSE	1.13	1.08	4.08
15	1129B04.BSE	1.23	1.17	4.56

2.2.2 Optimization

During the past quarter, we have worked on improving the program which will optimize the alcohol fuels blending facility. The primary focus was on calculating the manufacturing cost of the synthesis gas used to make the alcohols. We have transferred the information contained in our spreadsheet models for Case 5 into a FORTRAN subroutine that will be included as part of the optimization program. This gives us the freedom to look at more variables during the optimization. Most important among these are the desired synthesis gas flow rate, synthesis gas hydrogen-to-carbon monoxide ratio, and the synthesis gas recycle ratio in the alcohol synthesis reactor. Figure 2.3 shows some of the information we can obtain using the subroutine. This figure shows the manufacturing cost of the synthesis gas as a function of the desired flow rate. Being able to do this calculation for different conditions during the optimization will yield more accurate results.

In addition to the previously mentioned subroutine, we have also worked on improvements to the optimization algorithm. Two test problems have been found that are similar to the alcohol fuels blending facility. These test problems have known optimums. Using these problems, we are attempting to determine how to set up most efficiently the optimization algorithm for use on the alcohol fuels blending facility. The test problems have only recently been constructed, so no results are yet available as to the best optimization scheme.

2.3 Conclusions and Recommendations

The calculated and measured fuel to air ratios are in good agreement for different examined runs. Holding the total amount alcohol in the blends constant (10%), three blends are selected for future runs. These blends are chosen based on the oxygen percent by weight each blend contains.

The optimization routine will be ready when results for Task 1 are available.

2.4 Future Work

Different runs will be conducted using suitable blends. Engine knock limits and maximum spark advance for brake engine torque are to be determined. Different combustion characteristics are to be examined such as heat release, flame speed, and burned mass fractions.

For the upcoming quarter, we have the following goals. First, we will be analyzing the results from the test problems in order to set up the optimization on the alcohol fuels blending facility. Second, we will be constructing a general reaction subroutine for use in the program. Currently, we are using our own estimates for the products of reaction at differing feed conditions. Eventually, we will have data from Task 1 which would allow us to calculate the outlet compositions from the reactor as a function of temperature, pressure, hydrogen-to-carbon monoxide ratio, and feed rate. Our goal is to create a subroutine that will require only the coefficients to some equations to simulate the reactor products. These coefficients would be calculated using the data generated by Task 1. Third, we will be looking to improve the equations currently being used to calculate the equipment and utility costs in the alcohol fuels blending facility. Some of the equations were originally calculated in 1994. We will look into their accuracy, as well as developing other equations in place of estimates that are currently being used.

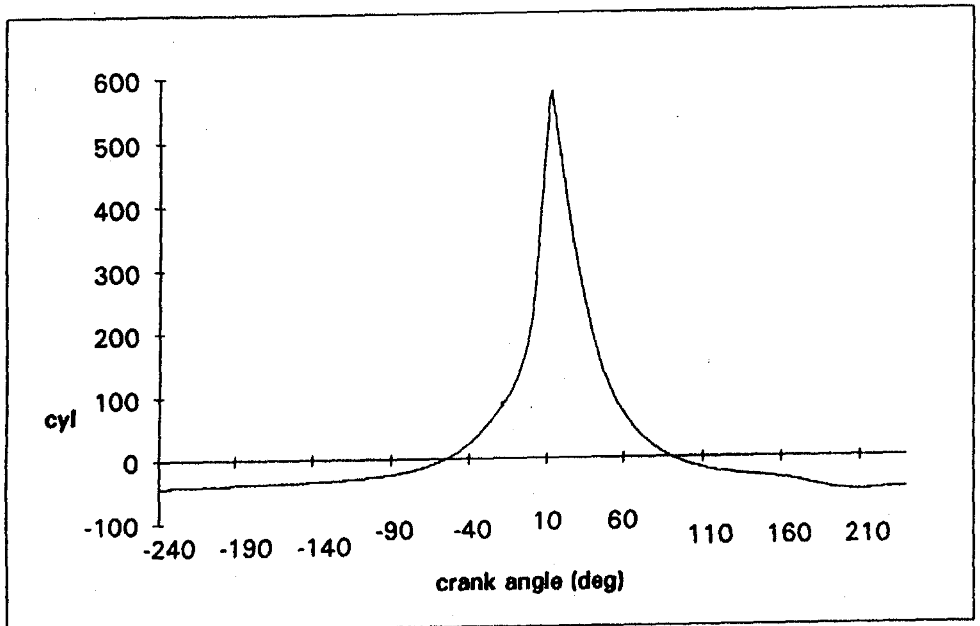

Figure 2.1a. In cylinder pressure trace (knocking cycle)

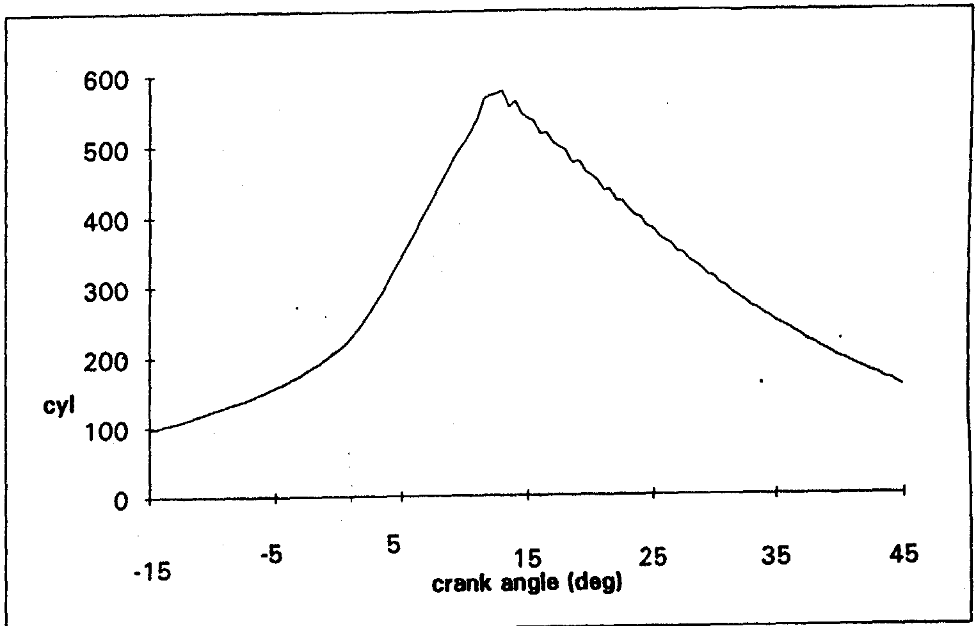

Figure 2.1b. Expanded in cylinder pressure trace (knocking cycle)

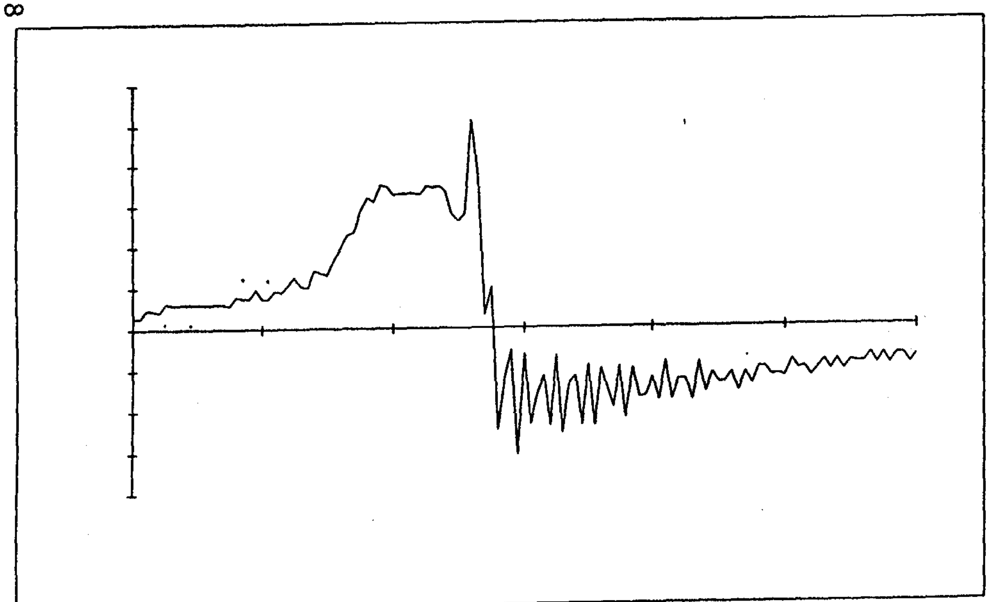

Figure 2.1c. First derivative of pressure trace (knocking cycle)

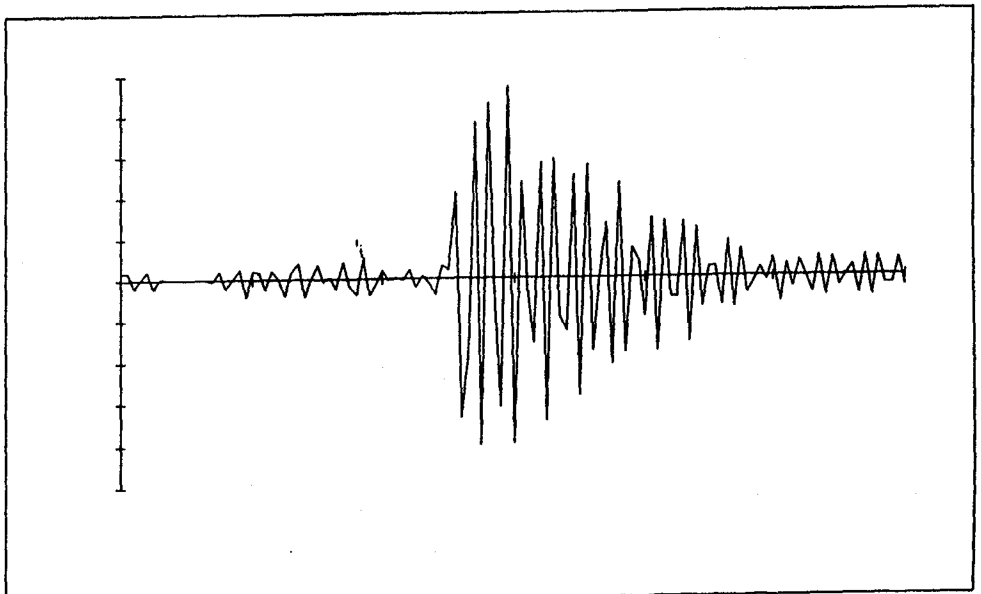

Figure 2.1d. Third derivative of pressure trace (knocking cycle)

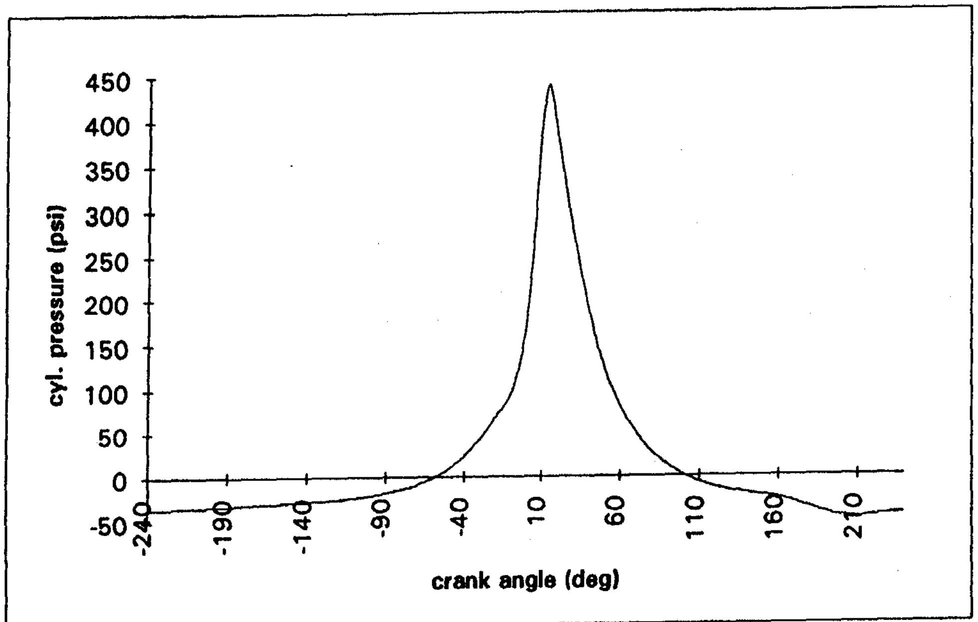

Figure 2.2a. In cylinder pressure trace (non-knocking cycle)

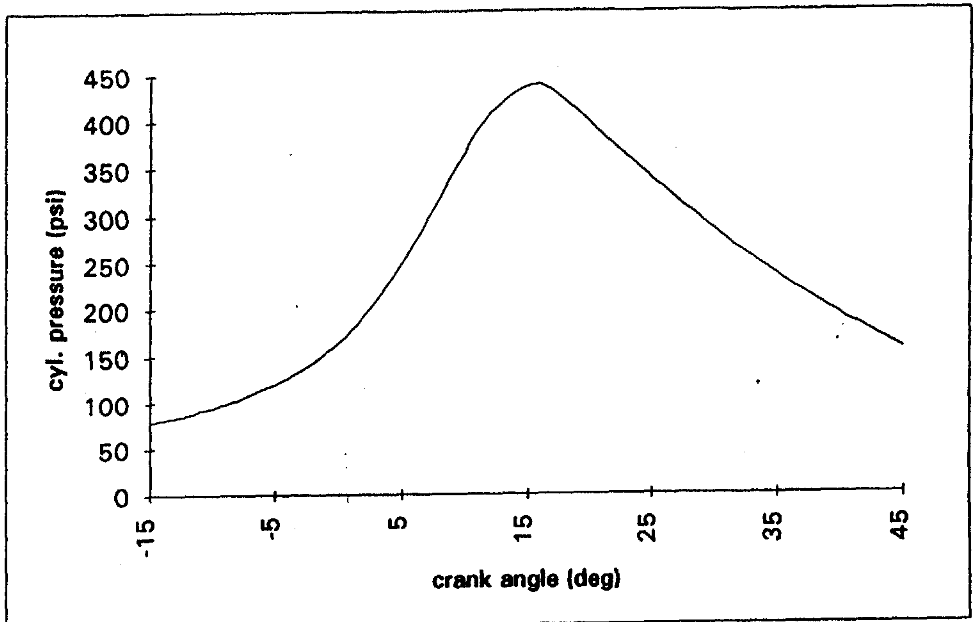

Figure 2.2b. Expanded in cylinder pressure trace (non-knocking cycle)

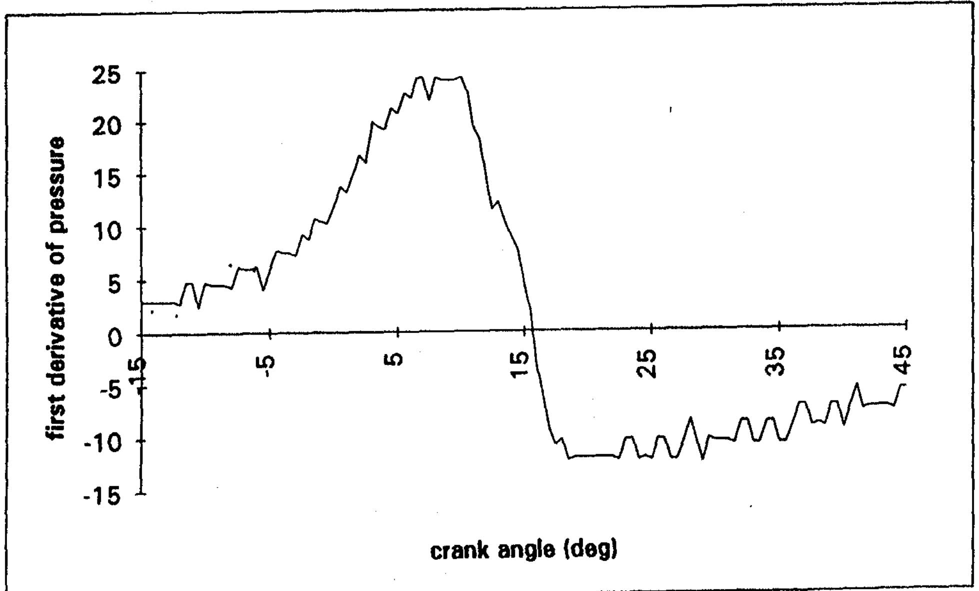

Figure 2.2c. First derivative of pressure trace (non-knocking cycle)

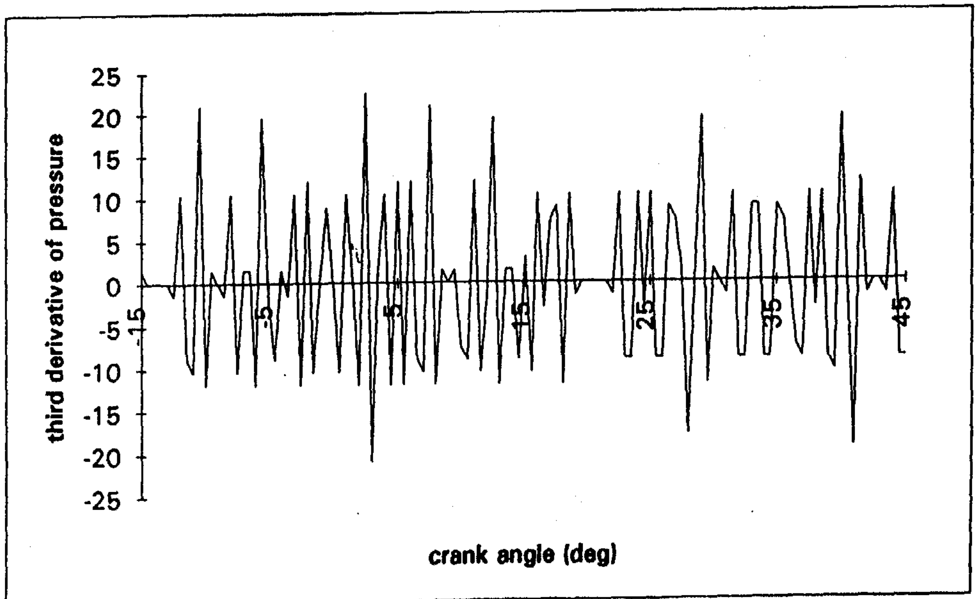

Figure 2.2d. Third derivative of pressure trace (non-knocking cycle)

Figure 2.3
Production Cost of Syngas at Varying Flow Rates and H2:CO Ratio of 1.1