

**CONVERSION OF METHANE TO METHANOL AND  
ETHANE TO METHANOL AND ETHANOL BY OZONE  
SENSITIZED PARTIAL OXIDATION AT NEAR  
ATMOSPHERIC PRESSURE**

by

GUOPING ZHU

A thesis

submitted to the Faculty of Graduate Studies in partial  
fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry  
The University of Manitoba  
Winnipeg, Manitoba

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## ABSTRACT

The reactions of methane-oxygen and ethane-oxygen mixtures with ozone as a sensitizer in the feed-gas were quantitatively studied at near atmospheric pressure in a dual-flow system. Ozone was generated by spark or silent discharge.

The effect of ozone sensitization was demonstrated and confirmed for both the methane-oxygen reaction and the ethane-oxygen reaction. The influences of reaction temperature, oxygen concentration in the feed-gas, residence time in the reactor, and ozone concentration in oxygen on both reactions were investigated. The results of the ozone sensitized reaction of methane with oxygen in three different reactors were compared.

For the methane-oxygen reaction, methanol selectivities between 7.0 and 54 %, with HCHO selectivities between 1.0 and 21 %, were observed for  $\text{CH}_4$  conversion equal to or less than 7.3 %. The selectivities of CO were found to be between 27 and 78 %, but the selectivities for  $\text{CO}_2$  were between 2.1 and 7.6 %.

For the ethane-oxygen reaction, ethanol selectivities between 3.95 and 21.76 % and methanol selectivities between 17.13 and 41.02 % with the combined formaldehyde-acetaldehyde-methanol-ethanol (FAME) selectivities between 36.7 and 95.7 % were observed for ethane conversion equal to or less than 6.1 %. The FAME selectivity was found to be over 90 % when the ethane conversion was below 3.5 %.

The reaction mechanism for both the methane-oxygen reaction and the ethane-oxygen reaction was proposed. At lower temperature, the reaction was initiated by ozone and at higher temperature the reactions proceeded by both the ozone initiated reaction and the ordinary homogeneous reaction.

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# **CHAPTER I**

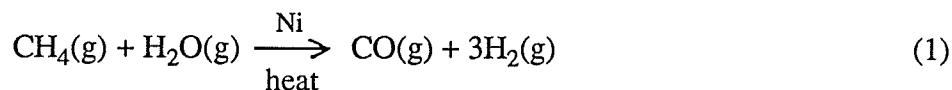
## **INTRODUCTION**

### 1.1. Introductory remarks

Reserves of natural gas are abundant in the world, especially in the Middle East, Canada, USSR and China. Direct utilization of natural gas is limited by inconvenience due to the problems of storage, transportation and handling. The conversion of natural gas into more valuable and more readily transportable fuels and chemical feedstocks has attracted great interest in recent decades. The principal product produced from natural gas at present is methanol, which is not only an important industrial chemical (ranked 22nd in the top 50 chemical products in the United States<sup>1</sup>), but also a more efficient automotive fuel than gasoline<sup>2</sup>. If methanol as transportation fuel is adopted even partially, a great increase in production will be required to meet the higher demand.

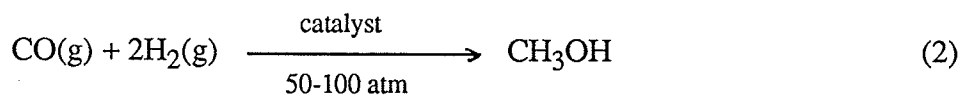
The existing commercial process for the production of methanol from natural gas (essentially methane) is a two-stage process.

Stage one: the intermediate formation of synthesis gas by the reforming reaction



$$\Delta H_1^\circ = 206.3 \text{ kJ/mol}$$

Stage two: the conversion of synthesis gas into methanol by a catalytic process



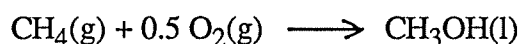
$$\Delta H_2^\circ = -90.8 \text{ kJ/mol}$$

The main disadvantage of this process is obvious from the energy balance calculation of the whole process. In the first stage, methane is extensively oxidized to carbon monoxide, but in the second stage the carbon monoxide is then reduced to methanol. Although the second reaction is exothermic, the total process is endothermic.

$$\Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = 206.3 - 90.8 = 115.5 \text{ kJ/mol}$$

In addition, since the conversion catalyst is easily deactivated by sulfur, chloride, and other poisons, the synthesis gas must be cleaned in order to get rid of these materials. Therefore, complicated engineering steps are required and operation expenses are high in this process.

A new technology, direct conversion of methane to methanol, has been developed, in which methanol is produced in one step.



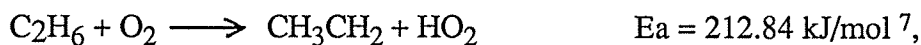
$$\Delta H^\circ = -128.4 \text{ kJ/mol}$$

A lot of research work on this process has been done in the last decade. Four independent comprehensive reviews<sup>3-6</sup> on this subject have appeared. The research work of Gesser and Hunter is in the frontier of this field.

Although the process of the direct conversion of methane to methanol is simpler and energetically more efficient than the conventional two-stage process, it is still necessary to operate at high temperatures, since methane is a very stable hydrocarbon, and at high pressure due to the consideration of thermodynamics and kinetics.

Methane and ethane are not chemically reactive substances. This is especially significant when methane is compared with the products obtained from its partial oxidation. In the reaction system the oxidation of the products will compete with the initial oxidation of methane or ethane. The desired products will be further oxidized to carbon monoxide and carbon dioxide. If the reactions are carried out at severe conditions, the selectivities will be reduced by the consecutive reactions of the desired products.

Since the activation energies of the reactions of methane with dioxygen and ethane with dioxygen are very high,



these reactions need catalysts or sensitizers to reduce the activation energies of the initiating reactions in order that the chain reactions that follow can proceed under mild reaction conditions.

Unfortunately, most of the catalysts studied led to greater amounts of combustion and actually resulted in lower methanol yields in the partial oxidation of methane than did reactions which were run in the absence of catalytic materials<sup>8</sup>.

Durante and coworkers<sup>9</sup> claimed that silicoferrate catalysts (crystalline silicometalates or zeolites with both iron and silicon incorporated in the structural framework) for methane oxidation appeared to stimulate greater rates and higher methanol selectivities by splitting the C-H bond of  $\text{CH}_4$  to generate higher desorbable methyl radical flux than observed in uncatalyzed vapor phase oxidations, but their highest selectivity of methanol obtained still did not reach that reported by Gesser et al.<sup>10</sup> in the direct homogeneous gas phase uncatalyzed partial oxidation of methane.

Omata and coworkers<sup>11</sup> found that the partial oxidation of methane could be sensitized by platinum wire placed upstream of a high pressure reactor. They believed that the radicals formed on platinum surface would be desorbed to initiate the vapor phase  $\text{CH}_4$ - $\text{O}_2$  reaction. Although the reaction temperature was lowered markedly (about 40 °C), the selectivity of methanol was not improved.

It has been shown<sup>12</sup> that a number of organic substances such as 2,3-dimethylbutane, which can more easily produce free radicals than methane, are able to sensitize the homogeneous oxidation of methane to methanol at high pressure through facilitating the formation of the free radicals involved in the oxidative chain processes. Though the reaction temperature and pressure can be lowered considerably by use of organic sensitizers with weaker C-H bond strength, this process is impractical from the point of economics due to the relatively high level of the sensitizers required and their net consumption.



If a cheap and easily available oxidizing reagent can be found which is more active than oxygen and can sensitize the reactions of methane and ethane with oxygen, then the reaction temperature and pressure could possibly be reduced. The reaction might be effectively carried out at atmosphere pressure. We believe that ozone is such an oxidizing reagent because ozone not only is cheap and can be easily produced *in situ* from oxygen by many methods, but it also can readily be decomposed into oxygen atom which can initiate the chain reactions leading to the formation of methanol and ethanol or other useful products.

## 1.2. Literature review

In 1898, Otto<sup>13</sup> first studied the reaction of methane and ethane with ozone at ordinary temperature and at 100 °C. Only qualitative results were obtained. In the case of methane, he detected formaldehyde and formic acid among the products of the reaction, and from the smell of the liquid, also inferred the presence of methanol. In the case of ethane, he proved the formation of acetaldehyde and acetic acid, but not of ethyl alcohol. He also discussed various forms of ozonizers.

In 1906, Drugman<sup>14</sup> investigated the oxidation of methane, ethane and ethylene by ozone at low temperature. Ozone was generated by silent discharge. 10~12 % Ozone was obtained when oxygen passed through four ozonizers. The reaction between methane and ozone was very slight at 15 °C but at 100 °C formaldehyde and formic acid were found in appreciable quantities. No methanol was detected. He thought that the reaction in the case of methane is so slow that any alcohol formed would be very rapidly oxidized to more stable formaldehyde. In the case of ethane, when the percentage of ozone was 2~3 per cent, acetaldehyde, acetic acid and ethanol and traces of formaldehyde were found in the products. Although the reaction with 10 % of ozone at 15 °C was much faster than in the case of methane, it was still slow. Ethanol, acetaldehyde, acetic acid and traces of hydrogen peroxide were detected. At 100 °C, the reaction was more rapid. The main

product was acetaldehyde. Ethanol was present in larger quantities than before, and traces of hydrogen peroxide were found. He concluded that ethanol was the first stage in the oxidation process and that acetaldehyde and acetic acid are secondary products of the reaction.

In 1922, Wheeler and Blair<sup>15</sup> first semi-quantitatively studied the action of ozone on methane. The ozonizer employed in their experiment gave approximately 4 % ozone from oxygen. Three series of experiments were done.

In the first experiments, mixtures of 97 % oxygen and 3 % methane were passed through the ozonizer and led into the reactor (heating period of 2.5 min). The reaction products were collected on the mixture of 50% glycerol and 50% water. The following results were obtained.

Temp. °C	mmg HCHO per litre of mixture used	HCOOH	mL CO <sub>2</sub> per litre of mixture used	% CH <sub>4</sub> → HCHO
15	0.3	trace		
100	0.8	trace	5	9
200	1.5	trace	7	14
300	2.2	trace	6	20
400	0.5	trace	5	9

They observed that at all temperatures the greater portion of the methane was oxidized into carbon dioxide, but no carbon monoxide was detected. Water was present in the products. It was found that at 15 °C the rate of reaction was very low and at above 400 °C all the ozone decomposed. The reaction rate and the rate of ozone decomposition increased with temperature.

In the second series of experiments, oxygen alone was passed through the ozonizer and methane was mixed with it before entering the reactor (about 20% methane in the mixture). The results were similar to those obtained in the first series.

In the third series of experiments, two parts of equal volumes of  $\text{NH}_3$  and  $\text{CH}_4$  were added to 5 parts of ozonized  $\text{O}_2$ . The  $\text{NH}_3$  was added to stabilize the formaldehyde as hexamethylenetetramine. They observed that the yield of formaldehyde was much the same as in the experiments without  $\text{NH}_3$  but the yield of formic acid was greatly increased to an amount equal to the formaldehyde. They did not detect methanol in any experiments.

The authors found that  $\text{NiO}$ -pumice,  $\text{Al}_2\text{O}_3$ -pumice,  $\text{Fe}_2\text{O}_3$ -pumice, Pt-asbestos, etc, accelerated the decomposition of ozone even below  $100^\circ\text{C}$  so that very little  $\text{CH}_4$  was oxidized.

In 1938, Soloveichik<sup>16</sup> reported the work on the incomplete oxidation of methane to  $\text{CH}_2\text{O}$  with 4~5%  $\text{O}_3$  at  $20^\circ\text{C}$ ,  $75\sim 80^\circ\text{C}$  and  $140\sim 5^\circ\text{C}$ . They found that the oxidation of methane and the formation of  $\text{CH}_2\text{O}$  was not catalyzed by Pt black, Cr-Ni or Pd on asbestos.

The oxidation of methane, propane, n-butane and isobutane with ozonized oxygen in the temperature range of  $25\sim 50^\circ\text{C}$  was investigated by Schubert and Pease<sup>17</sup>. Reaction rates were measured, *in situ*, in a temperature-controlled infrared absorption cell by observing the decrease of ozone concentration as measured by the absorption at  $1055\text{ cm}^{-1}$ . The rate dependence on ozone concentration for the reaction of methane, propane, n-butane and isobutane was shown to be first-order with respect to ozone by plotting the logarithm of the ozone concentration against time. The activation energies calculated on the basis of a first-order reaction with respect to ozone were 62.3, 50.6, 46.4, and  $43.1\text{ kJ}\cdot\text{mol}^{-1}$ , respectively. The order of reactivity was that which would be expected on the basis of the strengths of the C-H bonds involved. From the fact that the reaction of ozone with these low paraffins proceeded with a relatively low energy of activation, they assumed that an ozone molecule in low lying excited electronic state reacted with a hydrocarbon. The A

factors ( $7.2 \times 10^{10}$ ,  $3.1 \times 10^9$ ,  $8.2 \times 10^8$ , and  $4.4 \times 10^8 \text{ cm}^3.\text{mol}^{-1}\text{sec}^{-1}$ , respectively) were in the "normal range" for bimolecular reactions between complex molecules for the units involved.

They proposed the reaction mechanism based on their results:



HOO and ROO were presumed to be relative inert radicals at such a low temperature and were neutralized by recombination at the walls of the reactor.

For the reaction of methane with ozonized oxygen, the following results were obtained.

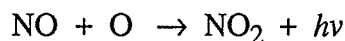
temp. °C	moles of products per moles of ozone consumed			
	HCOOH	CO <sub>2</sub>	CO	CH <sub>3</sub> OH
50	0.12	0.20	0.20	<0.02

On the basis of the investigation of the oxidation of isobutane with ozonized oxygen, Schubert and Pease<sup>18</sup> suggested that all oxidations by oxygen were initiated by small quantities of ozone always present and that they became self-sustaining at temperatures around 300 °C through regeneration of ozone by means of reactions such as the following one,

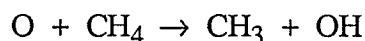


In 1956, Kleimenov and coworkers<sup>19</sup> reported their results of the study of methane oxidation with ozonized oxygen. They found that ozone began to decompose at about 100 °C. The primary oxidation products formed were peroxides. The peroxide formation was

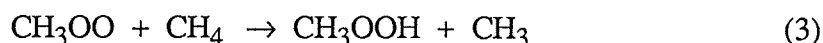
observed just from the beginning of the initial  $O_3$  decomposition. There was a maximum concentration of peroxide at about 200 °C. At lower temperatures where  $O_3$  did not thermally decomposed,  $CH_4$  was not oxidized. Oxygen atom formed during the thermal decomposition of ozone was identified by yellow-green luminescence after addition of NO into the reaction system.



They believed that the initiator of the reactions was oxygen atom and that  $CH_3$  and OH radicals formed by the reaction



were chain carriers. The following reaction mechanism was proposed:

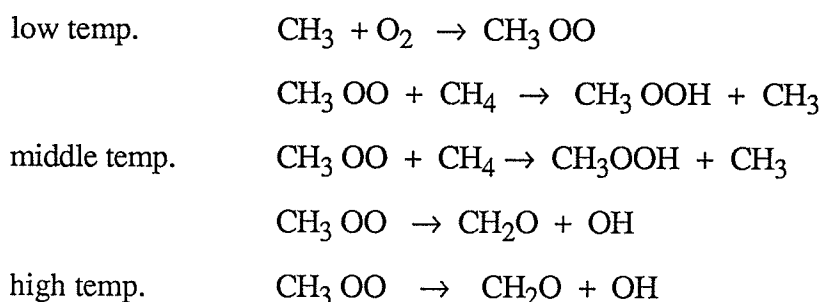


To determine the role of ozone in initiation of paraffin oxidation, Kleimenov and Nalbandyan<sup>20</sup> further studied the oxidation of propane and hydrogen in the presence of ozone. They found that ozone decomposed at 85 °C. Oxidation of hydrogen and decomposition of ozone began at the same temperature. The decrease in hydrogen oxidation was observed to be associated with the decrease in decomposition of ozone due to the change in contact time. The fact that the rate of reaction did not change in the presence of inert gases suggested that excited oxygen molecules did not play a significant role and that the initiation of the reaction was associated with oxygen atoms.

The results of investigation of the reaction between methane and oxygen atom formed by UV light at  $p=30$  mm Hg and  $t=20$  °C was also reported in the same article. For 75%  $CH_4$  + 25%  $O_2$  feedstock composition, 9%  $CH_4$  were converted to  $CH_3OOH$  and 7% to  $CH_2O$ . They concluded that  $CH_2O$  was a secondary product of the photochemical

decomposition of  $\text{CH}_3\text{OOH}$  on the basis of selectivity versus contact time. The dilution of the mixture by nitrogen did not change the rate of reaction so that initiation was attributed to atomic oxygen.

In 1958, Kleimenov and Nalbandyan<sup>21</sup> published their results of a study of the low-temperature oxidation of methane initiated by oxygen atoms formed in the thermal decomposition of ozone. A linear relationship was obtained at 150 °C between the yield of peroxide and the contact time for three different reaction mixture compositions. It was also found that the yield of  $\text{CH}_3\text{OOH}$  and  $\text{CH}_2\text{O}$  increased linearly with concentration of ozone at 150 °C and 180 °C but a linear relationship did not exist at temperatures higher than 200 °C. The yield of peroxide decreased with increase of oxygen concentration. The ratio of peroxide/formaldehyde depended on S/V ratio. They compared the experimental data with results obtained by photolyzing methane and found that the oxidation mechanism was the same except for the difference in the initiation radical (oxygen atoms and methyl radicals). They proposed the following mechanism for the photochemical methane oxidation:

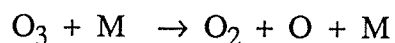


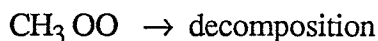
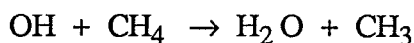
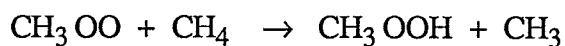
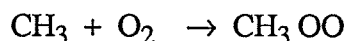
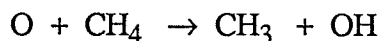
The kinetics of interaction of the  $\text{CH}_3\text{OOH}$  and  $\text{O}_3$  was studied by Kleimenov and Nalbandyan<sup>22</sup> under static conditions at 25~64 °C with  $\text{O}_3$  concentration being 5~6 times as much as the  $\text{CH}_3\text{OOH}$  concentration. The mixture of products was slowly passed through 2 traps, one at - 100 °C and the other at the temperature of liquid nitrogen. The product analysis indicated that the reaction proceeded chiefly with  $\text{CH}_3\text{OH}$  formation ( $\text{CH}_3\text{OOH} + \text{O}_3 \rightarrow \text{CH}_3\text{OH} + 2\text{O}_2$ ) and some  $\text{HCOOH}$ . The activation energy of the reaction was 29.3 kJ/mol.

Kleimenov et al<sup>23</sup> proved quantitatively that in the low temperature oxidation of CH<sub>4</sub> there were parallel reactions which led to the formation of aldehydes and peroxides. The rates of formation were determined for each substance by a radioactive indicator method.

Kleimenov and Markevich<sup>24</sup> used the differential calorimetry method to study the rate of O<sub>3</sub> thermal decomposition and CH<sub>4</sub> oxidation and found that the rate of O<sub>3</sub> thermal decomposition was uniform in a capillary with a uniform bore but when a capillary was used, the bore of which varied between 1 and 5 mm, breaks in the curve were observed at the widest cross-sections of the capillary. Methane oxidation in the non-uniform capillary was uniform. They concluded that the thermal decomposition of O<sub>3</sub> was a heterogeneous process, with the glass walls promoting the reaction, but CH<sub>4</sub> oxidation was a homogeneous reaction.

Oxidation of methane at low temperature with ozone as an initiator was comprehensively investigated by Kleimenov and Nalbandyan<sup>25</sup>. Two homogeneous initiation methods were used to elucidate the mechanism of CH<sub>4</sub> oxidation: (1) direct photochemical sensitization with Hg and (2) the addition of O<sub>3</sub>. Experimental work included (a) the reaction of CH<sub>3</sub>OOH with O<sub>3</sub>, (b) determination of the kinetics of CH<sub>4</sub> oxidation in the presence of small amount of O<sub>3</sub> added, (c) determination of the dependence of the yield of reaction products on the reaction temperature in the same reaction, (d) determination of the kinetics of product formation on the oxidation of CH<sub>4</sub> with O<sub>2</sub>, (e) determination of the relationship between the yield of reaction products and O<sub>3</sub> concentration in the initial mixture, (f) determination of the relationship between yield of CH<sub>3</sub>OOH and the composition of the CH<sub>4</sub>-O<sub>2</sub> mixture, and (g) determination of the effect of small additions of NO to the reaction mixture. They drew the conclusion that regardless of the nature of the initiating agent, the oxidation of CH<sub>4</sub> at low temperatures took place according to a chain reaction mechanism:





From this mechanism, expressions of the rate of formation of  $\text{CH}_3\text{OOH}$  and  $\text{HCHO}$  were obtained

$$d[\text{CH}_3\text{OOH}]/dt = k(\text{O}_3)(\text{M})(\text{CH}_4)$$

$$d[\text{CH}_2\text{O}]/dt = k(\text{O}_3)(\text{M})$$

The results of calculation agreed with the experimental data.

The reactions of ozone with ethane in the temperature range  $0^\circ\text{C}$  to  $60^\circ\text{C}$  were studied by Morrissey and Schubert<sup>26</sup> in 1963 in thermostated infrared gas cells. The major products of the reaction were carbon dioxide, water vapor, formic acid and methanol. In the presence of added oxygen, the activation energy for the ozone-ethane reaction calculated on the basis of the expression

$$-d[\text{O}_3]/dt = k[\text{O}_3] [\text{C}_2\text{H}_6],$$

was  $58.2 \text{ kJ/mol}$ . The pre-exponential term was  $1.24 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \text{ sec}^{-1}$ . In the absence of added oxygen, the activation energy was found to be  $61.5 \text{ kJ mol}^{-1}$  and the pre-exponential term was calculated to be  $3.50 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \text{ sec}^{-1}$ . No significant difference was determined between these values. The reactions were substantially independent of Pyrex and sodium chloride surfaces. An approximate equivalence was found between the number of gram-atoms of oxygen fixed in the products and the number of moles of ozone consumed. According to the low values obtained for the activation energy, they concluded that the initiating agent in the reaction was the ozone molecules because the activation energy of oxidation of ethane by dioxygen was between  $159$  and  $172 \text{ kJ} \cdot \text{mol}^{-1}$  <sup>27-30</sup>.

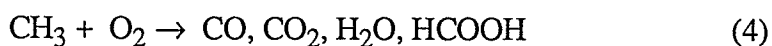
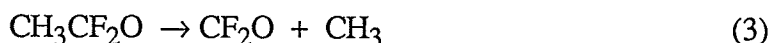
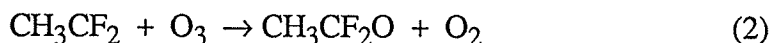
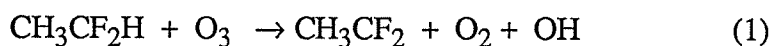


In 1974, Grodzitskii and Stadnik<sup>31</sup> reported that the addition of O<sub>3</sub> into O<sub>2</sub> had an insignificant effect on the kinetics of methane oxidation to HCHO and CO<sub>2</sub> in a fluidized aluminosilicate bed reactor.

In order to determine whether the reaction kinetics were affected by the presence of a strong electron-withdrawing atom in the molecule, Dilleuth and Lalancette<sup>32</sup> studied the reaction of ozonized-oxygen with 1,1-difluoroethane and 1,1,1-trifluoroethane in thermostated, infrared gas cells, in the temperature range 34~86 °C. The major products detected for 1,1-difluoroethane were carbon dioxide, carbon monoxide, carbonyl fluoride, acetyl fluoride, formic acid, acetic acid, and water. Formaldehyde was never observed. In the case of 1,1,1-trifluoroethane, the only reaction products observed were carbon dioxide, carbonyl fluoride, and formic acid. No carbon monoxide, formaldehyde, or trifluoroacetic acid was observed. Plots of the logarithm of ozone partial pressure vs time indicated that the reaction was first order with respect to ozone. The overall activation energy, calculated on the basis of the equation of

$$-d[\text{O}_3]/dt = k[\text{O}_3][\text{hydrocarbon}],$$

was  $66.1 \pm 1.7 \text{ kJ mol}^{-1}$  for 1,1-difluoroethane and  $73.2 \pm 2.1 \text{ kJ mol}^{-1}$  for 1,1,1-trifluoroethane. The pre-exponential terms were  $2.61 \pm 0.07 \times 10^8$  and  $6.34 \pm 0.24 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , respectively. The products observed suggested that the preferred site of initial ozone attack on 1,1-difluoroethane was the hydrogen attached to the fluorine-substituted carbon atom rather than the hydrogen of the methyl group. They proposed the following mechanism for 1,1-difluoroethane reaction.

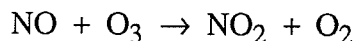
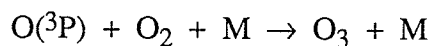
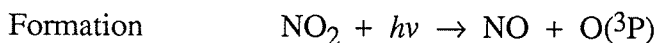
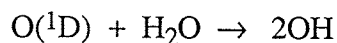
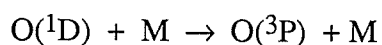
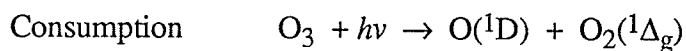


For the reaction of 1,1,1-trifluoroethane, they believed that the following step was involved in the mechanism.



Formaldehyde produced was rapidly oxidized to carbon dioxide.

The kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmosphere conditions were reviewed by Atkinson and Carter<sup>33</sup> in 1984. The major processes of consumption and formation of ozone in the atmosphere were summarized as:



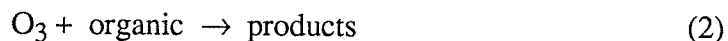
Two experimental techniques in kinetics studies of ozone reaction were discussed in detail.

(1) Absolute rate constant techniques

(a) Static and stopped-flow system

This was the most widely used method. Ozone reaction kinetics was determined by observing the rates of decay of  $\text{O}_3$  and/or the organic compound in a static system where the concentration of the other reactant was known.

$\text{O}_3$  was consumed by



$$-\text{d}[\text{O}_3]/\text{dt} = (k_1 + k_2[\text{organic}]) [\text{O}_3]$$

Under the condition that excess organic concentration was used, pseudo-first order decay of  $\text{O}_3$  should be observed.

## (b) Flow systems

## (i) Conventional flow systems

The rate constants could be calculated by the equation

$$k = \frac{\ln ([O_3]_{t_0} / [O_3]_t)}{0.5 ([organic]_{t_0} + [organic]_t) (t - t_0)}$$

based on the assumption of perfect plug-flow conditions. However, if axial diffusion was nonnegligible, an erroneously high rate constant would be obtained.

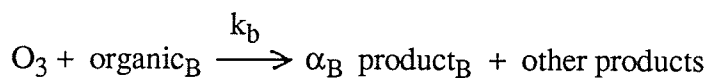
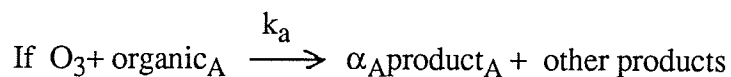
## (ii) Stirred flow reactor systems

The rate constant could be obtained from the expression

$$k = \frac{F}{V} \frac{([organic]_{t_0} - [organic]_f)}{[O_3]_f [organic]_f} = \frac{F}{V} \frac{([O_3]_{t_0} - [O_3]_f)}{[O_3]_f [organic]_f}$$

## (2) Relative rate constant technique

This technique is based on monitoring the yields of the major products from two organic reactants in the presence of  $O_3$ .



and if  $[organic] \gg [O_3]$ ,

$$\frac{\Delta[\text{product}_A]}{\Delta[\text{product}_B]} = \frac{k_a \alpha_A [organic_A]}{k_b \alpha_B [organic_B]}$$

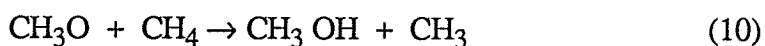
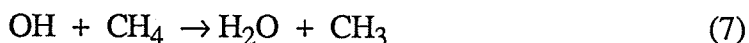
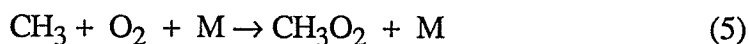
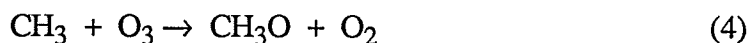
If  $\alpha_A/\alpha_B$  is constant, plots of  $\Delta[\text{product}_A]/\Delta[\text{product}_B]$  against  $[organic_A]/[organic_B]$  should yield straight lines of slope  $k_a \alpha_A / \alpha_B k_b$ , then  $k_a/k_b$  may be derived.

For the reaction of  $O_3$  with methane and ethane, Atkinson and Carter discussed the possibility of the molecular reaction of ozone with methane or ethane proposed by Schubert et al.<sup>17, 18, 26</sup>. They believed that at that time, it appeared that there was no evidence for an elementary reaction between  $O_3$  and the alkanes. They suggested that the rate constants obtained by Schubert et al were upper limits.

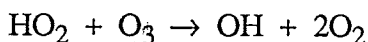
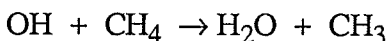
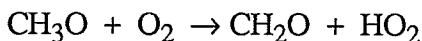
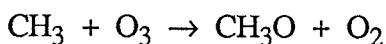
Rotzell<sup>34</sup> used a molecular beam source reactor which consisted of a heated 1 mm diameter alumina flow tube with a 0.2 mm nozzle to study the reaction of methane with ozonized oxygen. The product gas mixture expanding from the reactor was transformed into a molecular beam and analyzed by a mass spectrometer. The products detected at reaction pressure of about 600 m-bar and residence time 16 m-sec and reaction temperature range 480~830 °K were  $H_2O$ ,  $CO$ ,  $CH_2O$ ,  $CH_3OH$ ,  $H_2O_2$ ,  $CO_2$ , and  $CH_3OOH$ . It was found that experimental results could be fairly well modeled by a reaction mechanism consisting of 47 elementary reactions with 21 species. They concluded that the reaction was initiated by the thermal decomposition of ozone and very important in the reaction were secondary reactions of ozone with methyl radical and hydrogen atoms. Radical-radical reactions of methyl and methylperoxyl radicals were believed to play a dominant role in the course of the reaction.

The reaction of methane with decomposing ozone in the temperature range 75-175 °C and at below atmosphere pressure was investigated by Toby<sup>35</sup> in a static system based on a thermostated cylindrical quartz cell. An unusual and reproducible period of induction was observed followed by a rapid depletion of  $O_3$ . The reactions were simulated by a 70-step mechanism which could qualitatively account for the period of induction. It was observed that the reaction was slowed by addition of  $O_2$ . It was found that the following simpler 10-step mechanism could be used to account quantitatively for the kinetics of inhibition with added oxygen.

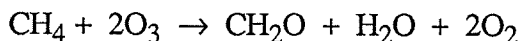




They proposed the main ozone-destroying chain based on the simulation and experimental results is as follows:



The overall reaction for the major ozone-destroying steps was



No evidence was found for a molecular reaction between  $\text{CH}_4$  and  $\text{O}_3$ .

Recently, Gesser et al.<sup>36</sup> showed qualitatively that ozone could sensitize the partial oxidation of both methane and ethane with dioxygen.

### 1.3. Objectives

The objective of this research was to develop a new process for the conversion of methane and ethane to methanol, ethanol and other valuable chemicals at atmospheric pressure. Specially, the following questions were investigated.

- Can ozone sensitize the reaction of methane and ethane with oxygen at about 1 atm pressure?

- At what temperature of reaction can the effect of sensitization begin to be observed?
- What kind of reactor material is suitable for this process?
- What kind of method of ozone generation is suitable for this process?
- What are the relationships between the selectivities and yields of products and the conversions of reactants, reaction temperature, residence time and oxygen concentration in the feed-gas mixture?
- What is the difference of reactivity between methane and ethane under ozone sensitization condition?

## **CHAPTER II**

# **EXPERIMENTAL**

## 2.1. Ozone generation and analysis

### 2.1.1. Analysis of ozone

Several methods<sup>37</sup> can be used for the analysis of ozone. The iodometric method, however, seems to be quite simple and reasonably accurate in determining the concentration of ozone by comparison with other methods, so this method was used in this research for measurements of ozone concentration. In this method ozone reacted with iodide in a buffered solution to produce iodine, the concentration of which was determined by a spectrophotometric method. Based on the stoichiometry of the reaction between ozone and iodide, the concentration of ozone was obtained by calculation from the concentration of iodine detected.

#### Preparation of ozone detection solution

Saltzman and Gilbert<sup>38</sup> showed that the pH value of the iodide solution had a great effect on the accuracy of the determination of the concentration of ozone. No iodine was liberated by ozone in strong alkaline iodide solution. The concentration of ozone obtained in acidic iodide solution was found to be greater than the real value of the concentration of ozone. The concentrations of iodide and the concentration of buffer materials influenced the coloring time and therefore influenced the accuracy of the analysis in this method. A 1% potassium iodide, neutral phosphate-buffered ozone detection solution was used in this research because it was shown<sup>38</sup> that it had good stability, a stable final iodine color and a stoichiometry very close to  $O_3 = I_2$  as shown by comparison with other independent methods. The neutral, phosphate-buffered iodide ozone detection solution (referred to as Solution A) was prepared by the following procedure:

13.62 grams of potassium dihydrogen phosphate, 14.20 grams of anhydrous dibasic sodium phosphate, and 10.0 grams potassium iodide were successively dissolved in



distilled water and then distilled water was added to the mixture to make 1 liter of solution.

The concentration of the solution obtained was:

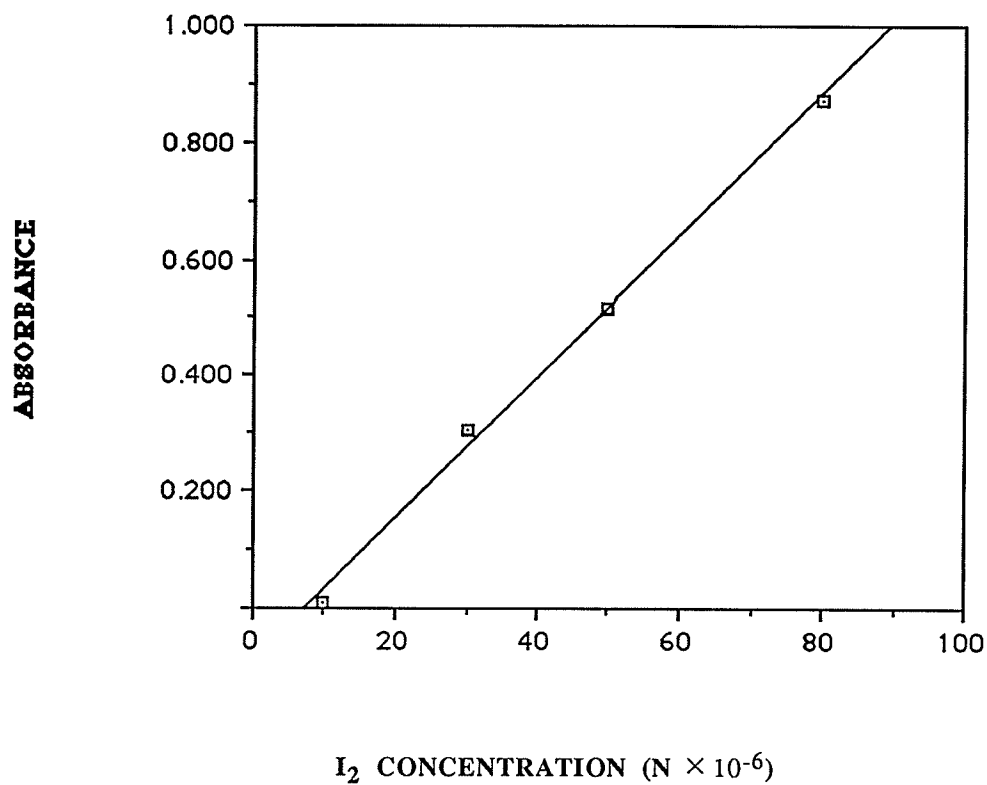
1% KI, 0.1 M  $\text{KH}_2\text{PO}_4$ , 0.1 M  $\text{Na}_2\text{HPO}_4$ .

Determination of the concentration of iodine liberated by ozone

0.01 N Iodine solution (1.27 grams of iodine and 16 grams of potassium iodide per liter) was prepared and standardized by thiosulphate through titration using starch as indicator. The iodine solution was diluted with Solution A to form a standard series, and read on a Beckman DK-2A Ratio Recording Spectrophotometer at 349 m $\mu$  at which the maximum absorption of iodine was observed. The absorbances (the blank was Solution A and the path length of the cell was 1 cm) of the standard solution series obtained were given in Table 2.1-1.

Table 2.1-1. The absorbances of the standard  $\text{I}_2$  solution series

$\text{I}_2$ conc. ( $\text{N} \times 10^{-6}$ )	absorbance
10	0.007
30	0.306
50	0.517
80	0.873



$\lambda = 349 \text{ m}\mu$

sensitivity = 3

time constant = 0.1

scanning time = 20 min.

scale expansion = 2x

photomultiplier = 1x

Figure 2.1-1. Relationship between absorbance and concentration of I<sub>2</sub> in solution.

The absorbance was plotted graphically versus concentration of iodine in the solution and a straight line was obtained (Figure 2.1-1). The following equation was derived from the graph of the absorbance versus concentration of iodine:

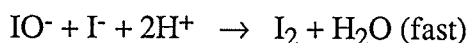
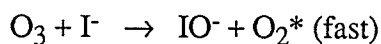
$$y = 7.672 + 81.81 x$$

where y is iodine concentration ( $10^{-6}$  N) and x is absorbance. The cause why the intercept was not zero is unknown, but this did not influence the results obtained.

The absorbances of the unknown iodine solutions were measured at the same conditions as the standard iodine solutions and the concentration of iodine in the unknown sample was determined by comparing its absorbance with the absorbance of the known concentration of the standard iodine solution or by substituting its absorbance for x in the equation obtained and calculating the y.

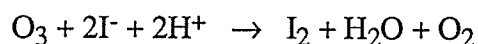
#### Procedure for the measurement of ozone concentration

The gas sample containing ozone was passed through 20 mL of Solution A in an ozone detection tube with a very fine porous fritted gas distribution disc at the lowest part of the iodide solution to improve the efficiency for the absorption of ozone. When ozone was passed through the iodide reagent, it was completely absorbed and reacted with iodide immediately. Most of the iodine (> 90 %) was liberated instantly by the following scheme:



where  $\text{O}_2^*$  is dioxygen in an excited state.

The total reaction was



The gas sample size was determined by means of a stopwatch and a soap bubble flowmeter. The iodine solution obtained was kept for 20 minutes to allow for complete

color development. The solution was diluted with Solution A to the proper concentration range, which fell within the range of the standard series of iodine solution, and measured at 349 m $\mu$  on the Beckman DK-2A Ratio Recording Spectrophotometer in an 1 cm cell.

### **2.1.2. Ozone generation by the spark method**

The apparatus for generation of ozone by the spark method and the circuit for the pulsed power supply are shown schematically in Figure 2.1-2a and Figure 2.1-2b, respectively.

The line from the oxygen cylinder [1] to the SS (stainless steel) block [3] was constructed with 1/8" copper tubing. The connection from the SS block [3] to the ozone detection solution tube [4] was made with silicon rubber tubing. And the connection from the ozone detection solution tube [4] to the soap film flowmeter [5] was made with ordinary rubber tubing.

The induction coil [6] could produce 50 kV pulse which made the plug [7] generate the spark.

The flow rate of the oxygen gas was controlled by the vernier valve [2].

An oxygen stream from the oxygen cylinder [1] was allowed to pass through the SS block where the oxygen was exposed to the electric spark produced by the spark plug in the SS block and was partially converted to ozone. The O<sub>2</sub> and O<sub>3</sub> gas mixture was then passed through Solution A in the ozone detection tube. The ozone generated was analysed by the method described above.

### **2.1.3. Ozone generation by the silent discharge method**

The apparatus for the generation, detection and measurement of ozone by silent discharge is shown schematically in Figure 2.1-3a.

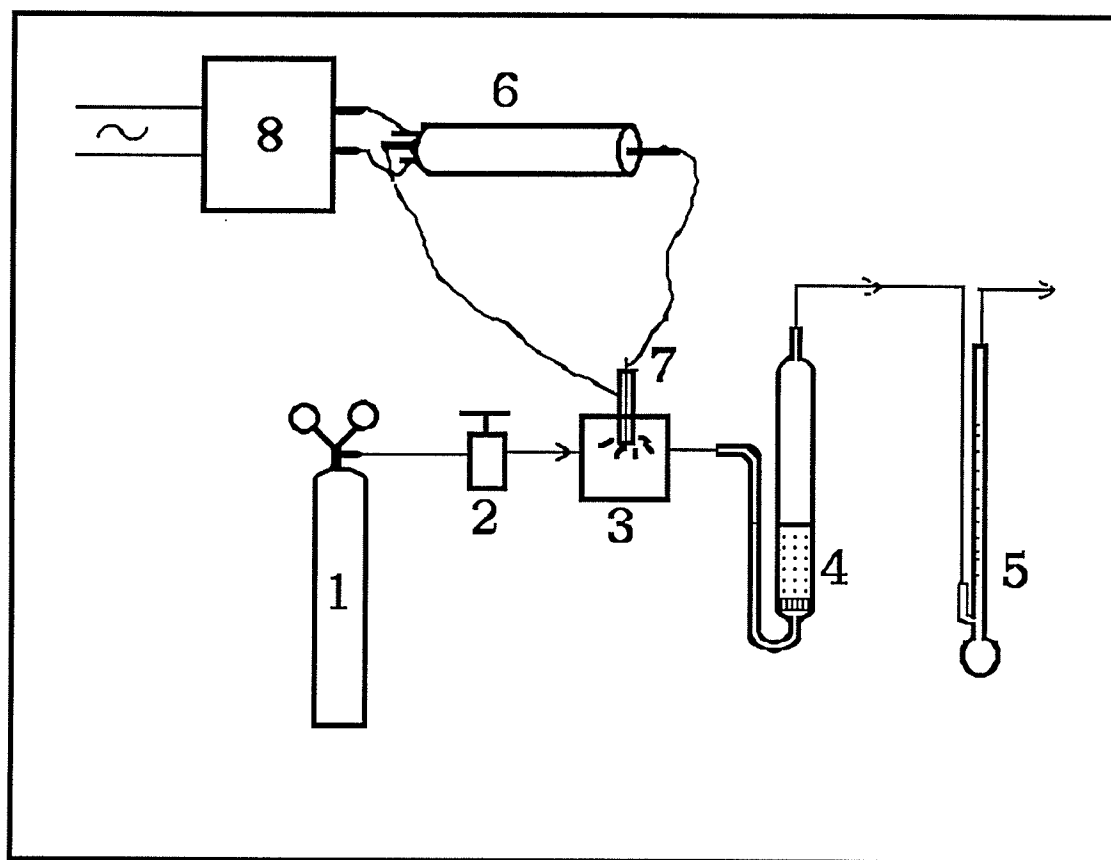


Figure. 2.1-2a. Apparatus for generation and detection of ozone by the spark method

- |                               |                                  |
|-------------------------------|----------------------------------|
| 1. Oxygen cylinder            | 2. Vernier valve                 |
| 3. SS (stainless steel) block | 4. Ozone detection solution tube |
| 5. Soap film flowmeter        | 6. Automobile induction coil     |
| 7. Spark plug                 | 8. Pulsed power supply           |

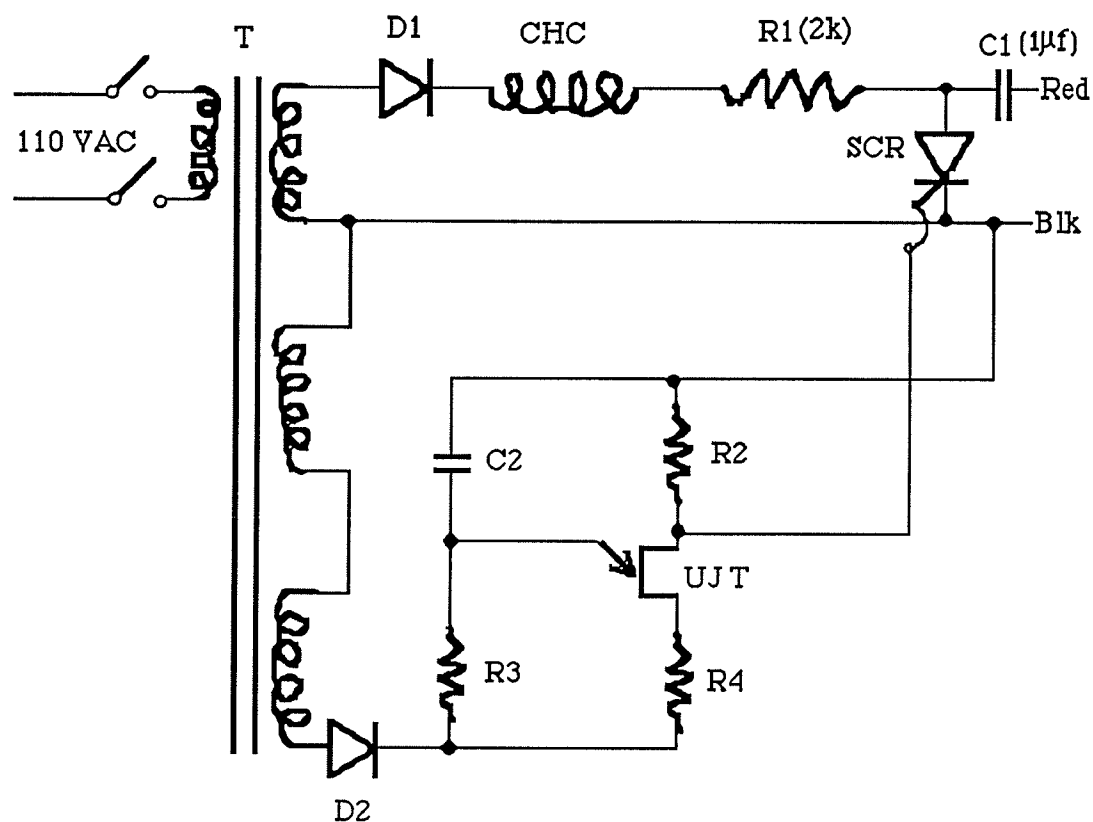


Figure 2.1-2b. The circuit of the pulsed power supply

T: Transformer

D1 & D2: Diode

CHC: Choke coil

C1 & C2: Capacity

SCR: Silicon controlled rectifier

UJT: Unijunction transistor

R1, R2, R3 & R4: Resistant

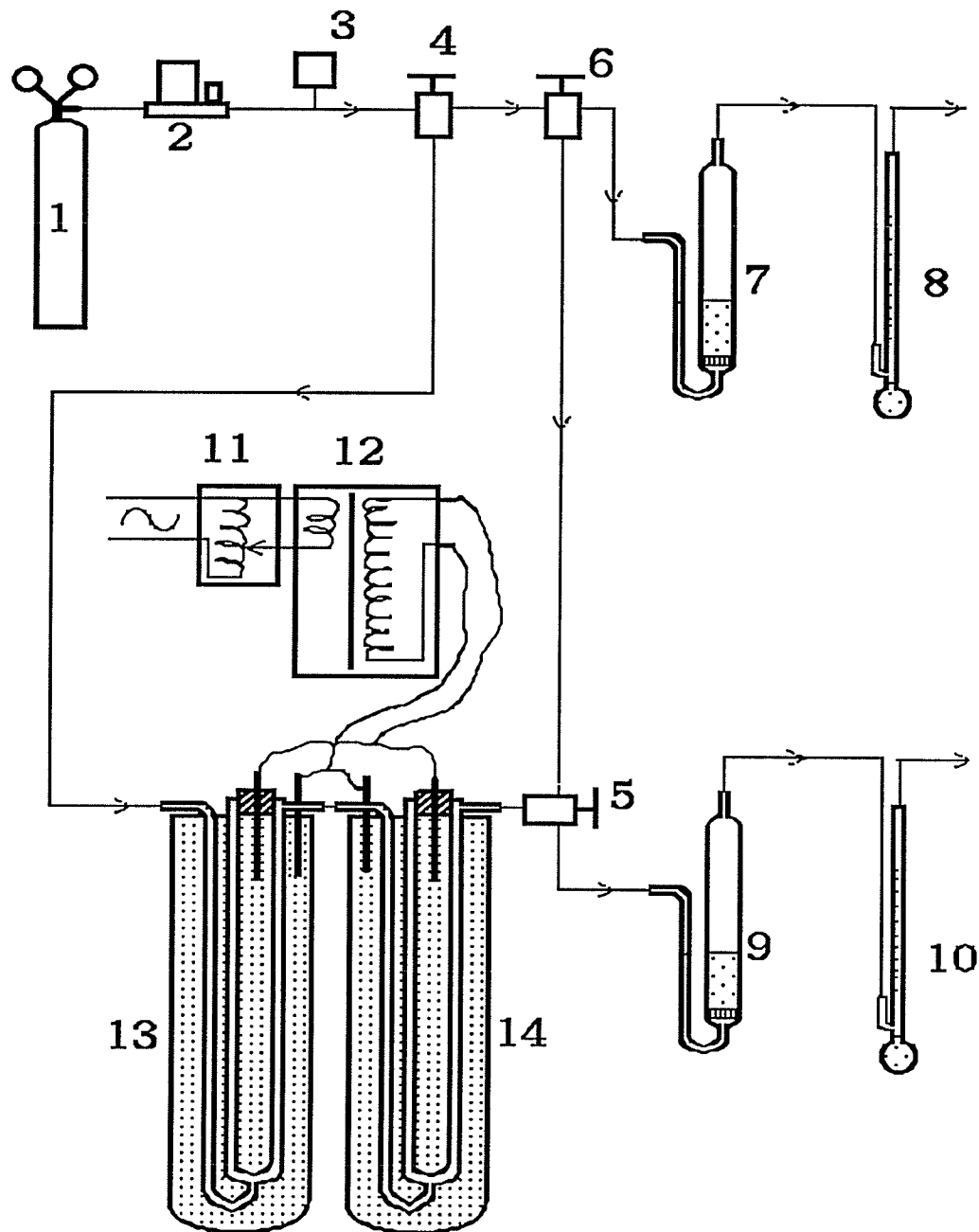


Figure 2.1-3a. Apparatus for generation and detection of ozone by silent discharge

- |                              |  |                               |
|------------------------------|--|-------------------------------|
| 1. Oxygen cylinder           | 2. Mass flow controller                          | 3. Pressure transducer        |
| 4. Three-way valve           | 5.&6. Three-way cock                             | 7. Back-pressure control tube |
| 8&10. Soap bubble flowmeter  | 9. O <sub>3</sub> detection solution tube        | 11. Variac                    |
| 12. High voltage transformer | 13&14. Silent discharge O <sub>3</sub> generator |                               |

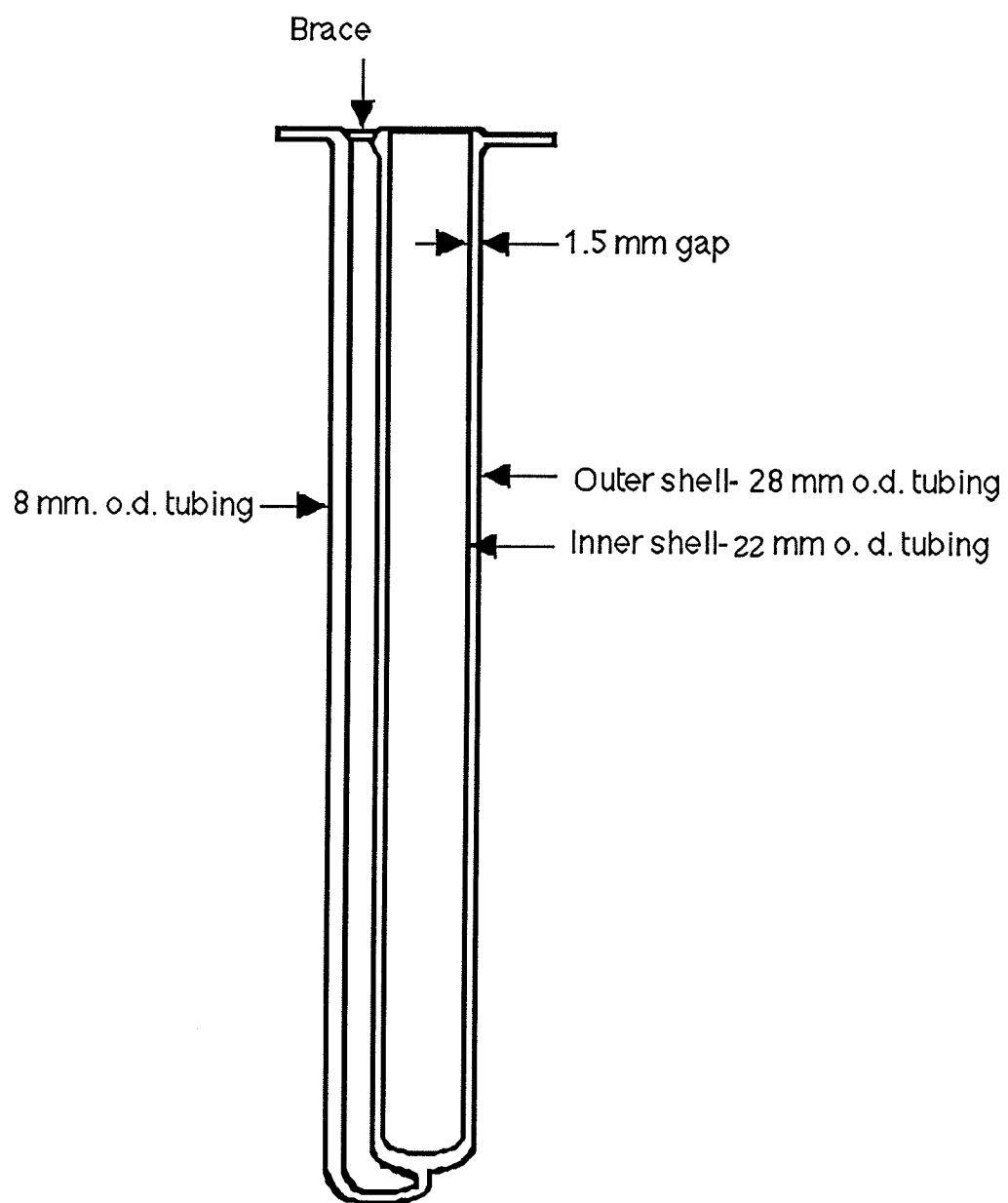


Figure 2.1-3b.

Berthelot ozonizer tube



The ozone generator used in Reaction System III consisted of a series of two Pyrex glass Berthelot ozonizer tubes<sup>39</sup> (54.5 cm and 63.5 cm long) (Figure 2.1-3b) immersed in saturated  $\text{Na}_2\text{SO}_4$  solution baths (o.d. 50 mm), respectively (Figure 2.1-3a). The Berthelot ozonizer had two tubes (the inner tube (o.d. 22 mm) and the outer tube (o. d. 28 mm)) and there was a 1.5 mm narrow annular space between the two tubes which allowed the oxygen gas or oxygen-ozone mixture to flow. The inner Berthelot ozonizer tube was filled with the same solution (saturated  $\text{Na}_2\text{SO}_4$  solution) as the bath. Two copper electrodes were immersed in the solution in the inner tube and in the solution in the bath (Figure 2.1-3a), respectively. These electrodes were connected to the terminal of the high voltage transformer [12] which could raise the input voltage of 115 V (current 2.38A) to about 15 kV. The voltage charged on the electrodes of the ozone generators were controlled by the Variac [11] in Figure 2.1-3a.

The ozone detection solution tube [9] and the back-pressure control tube [7] had almost the same dimensions and were constructed from the same material (Pyrex glass for the tube and fritted glass for the distribution disc). The ozone detection solution tube contained 20 mL of Solution A, but the back-pressure control tube contained 20 mL of water to keep the back-pressure before the tube almost the same as that before the ozone detection solution tube.

Oxygen flow rate was controlled by the mass flow controller [2] (Brook 5850) and measured by the soap bubble flowmeter [8] and a stopwatch.

#### 2.1.4. Experimental procedure

Pure oxygen gas from the cylinder [1] flowed through the mass flow controller[2], through the three-way valve [4], then passed through the two consecutive ozone generators and reached the three-way cock [5]. The oxygen then passed through three-way cock [6], the back-pressure control tube [7] and reached the soap bubble flowmeter[8] before going to the vent. When the flow rate was controlled at the desired value and became stable, the

flow rate was measured by the stopwatch and the soap bubble flowmeter [8]. After the oxygen gas completely replaced the air in the two ozone generator (the time required depended on the oxygen flow rate; if the flow rate of oxygen gas was 10 mL/ min, it usually required 1 hr to replace the air in the generators), the ozone generation was started. The high voltage (over 10 kV) was charged on the electrodes of the two ozone generators. The oxygen was partially converted to ozone by the silent discharge when oxygen molecules flowed consecutively through the 1.5 mm narrow gaps between the inner and the outer tubes in the two Berthelot ozonizers. After the ozone concentration in the mixture of ozone and oxygen coming from the last ozone generator was stable (about 1 hr when the flow rate oxygen gas was 10 ml/min), the three-way cock [5] was switched to change the flow direction of the gas mixture of ozone and oxygen to go to the ozone detection solution tube [9]. At the same time the stopwatch was started to record the time passed. As the mixture of the ozone and oxygen passed through the ozone detection solution (Solution A), ozone was absorbed and immediately reacted with iodide and liberated iodine. When the solution became dark enough, the three-way cock [5] was switched and the flow of the gas mixture from the ozone generator [14] was stopped and at the same time the stopwatch was stopped, and the sampling time was obtained. At the same time the direction of the flow of oxygen gas from the mass flow controller [2] was changed at the three-way valve [4] to go directly to the three-way cock [6] and then to the back-pressure control tube [7]. The silicon rubber tube connecting the two three-way cocks [5] and [6] was disconnected just at the three-way cock[5] and the pure oxygen was allowed to flow through this section of the silicon rubber tube to wash out the ozone remaining in the tube. Then the silicon rubber tube was connected again and the flow direction in the three-way cock [5] was changed to allow the pure oxygen gas to wash the ozone remaining in the tube between the three-way cock [5] and the ozone detection solution tube [9] into the ozone detection solution. During the sampling the flow rate could be checked by the soap bubble flowmeter [10].

The iodine solution in the ozone detection solution tube [9] was kept for 20 minutes for complete color development and then it was diluted to the proper concentration. Its concentration was measured by the method mentioned before.

The concentration of ozone in the mixture of ozone and oxygen coming from the last ozone generator was then calculated.

## 2.2. Reaction system

### Incorporation of nitrogen into the methane cylinder

Nitrogen was incorporated into the methane cylinder (Figure 2.2-1) as an internal standard for calculating the mass balance in the partial oxidation of methane.

The incorporation line was constructed from 1/8" stainless steel fittings and tubings. The pressure in the nitrogen cylinder was higher than that in the methane cylinder. The check-valve [4] prevented the backflow of the contents in the methane cylinder so that only nitrogen was permitted to flow into methane but not *vice versa*.

The incorporation line was evacuated before the addition of nitrogen. The crude concentration of nitrogen in the methane cylinder was estimated, during the incorporation process, by monitoring the pressure reading in the pressure gauge [6] (initial 1720 psig, and final 1770 psig). After incorporation the methane cylinder was rolled for 3 hr and left to lie on the floor over-night before use.

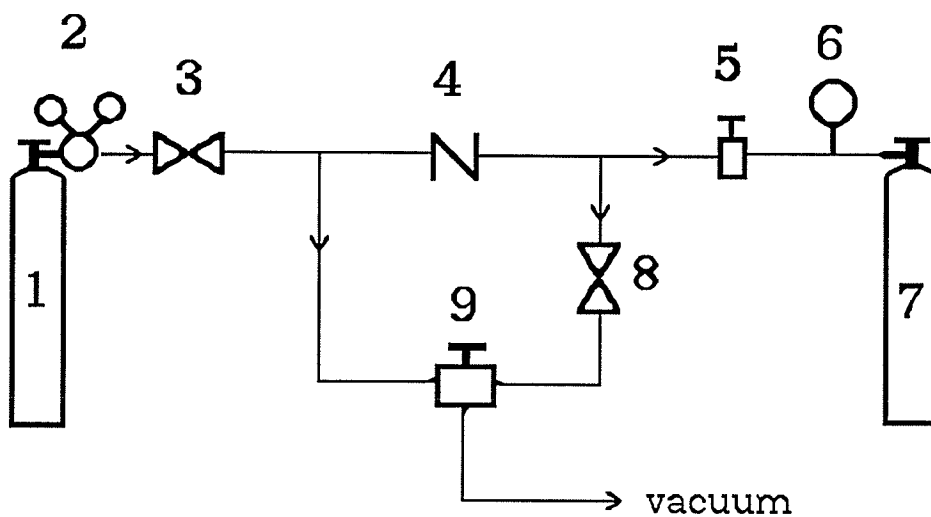


Figure 2.2-1. Incorporation of nitrogen into methane

- |                       |                            |
|-----------------------|----------------------------|
| 1. Nitrogen cylinder  | 2. High pressure regulator |
| 3 & 8 Shut-off valves | 4. Check-valve             |
| 5. Needle valve       | 6. Pressure gauge          |
| 7. Methane cylinder   | 9. WHITEY three-way valve  |

### 2.2.1. The reaction system with a steel reactor (Reactor I) (referred to as System I)

The reaction system with a steel reactor is shown schematically in Figure 2.2-2. It consisted of five sections: (a) reactor section, (b) ozone generation section, (c) input line section, (d) output line section and (e) analysis section.

(a) The reactor (Figure 2.2-3) consisted of a 355 mm  $\times$  21.4 mm o.d. (i.d. 14.4 mm) 316 stainless steel tube into which a Pyrex glass tube of 339 mm  $\times$  13.3 mm o. d. was inserted to form a close fit.

The reaction tube was heated over 300 mm of its length by two tube furnaces (Figure 2.2-3). The first heated a 150 mm pre-reaction section (the upper part of the reactor) and the second heated the remaining 150 mm of the reaction section (the lower part of the reactor). The temperature of the pre-reaction section was measured and monitored by a quick disconnect subminiature Chromel-Alumel thermocouple probe with 1/32" diameter 304 SS sheath (OMEGA ENG. INC). The temperature of the reaction section was measured and monitored by a similar thermocouple probe but with 1/16" diameter sheath. The two thermocouple probes were inserted into the reactor from the upper end and the lower end of the reactor through CONEX connections. Their hot junctions were kept in the middle of the pre-reaction section and the middle of the reaction section and their outputs were connected to two OMEGA Digital Temperature Controllers (model CN 300 KC) which controlled the two tube furnaces via two Variacs. Thus, the two sections of the reactor were temperature controlled. The temperatures of the two section could be read directly from the LCD displays of the two temperature controllers.

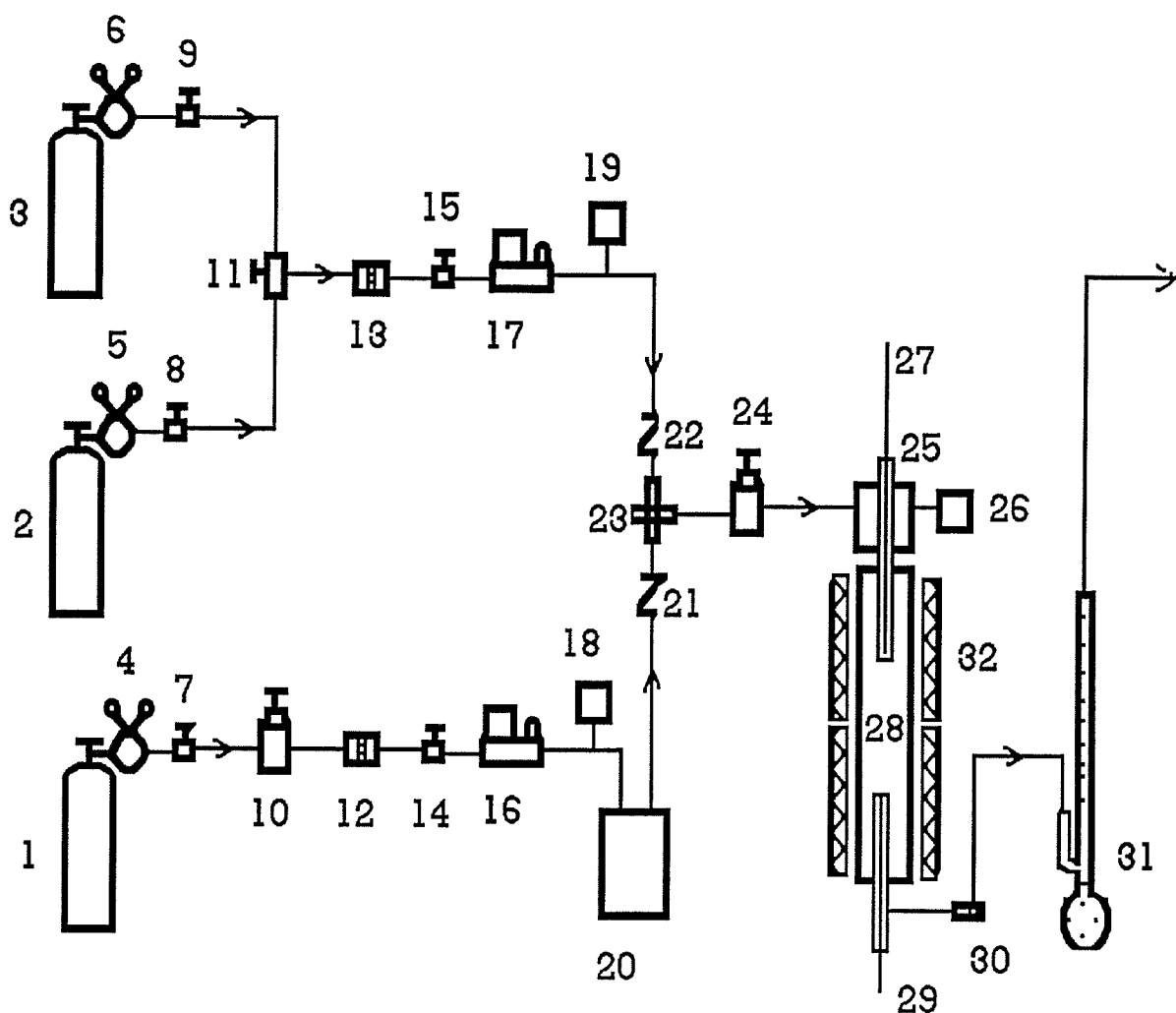


Figure 2.2-2. The reaction system with a steel reactor (Reactor I)

- |                                   |                                     |
|-----------------------------------|-------------------------------------|
| 1. O <sub>2</sub> cylinder        | 2. CH <sub>4</sub> cylinder         |
| 3. N <sub>2</sub> cylinder        | 4, 5, & 6. regulators               |
| 7, 8, 9, 14, & 15 shut-off valves | 10. vernier needle valve            |
| 11. three-way valve               | 12 & 13. filters                    |
| 16 & 17. mass flow controllers    | 18, 19 & 26. pressure transducers   |
| 20. ozone generator               | 21 & 22. check valves               |
| 23. mixing cross                  | 24. vernier needle valve            |
| 25. six-port SS block             | 27 & 29. thermocouple probes        |
| 28. reactor                       | 30. sampling port at 1 atm pressure |
| 31. soap bubble flowmeter         | 32. tube furnace                    |

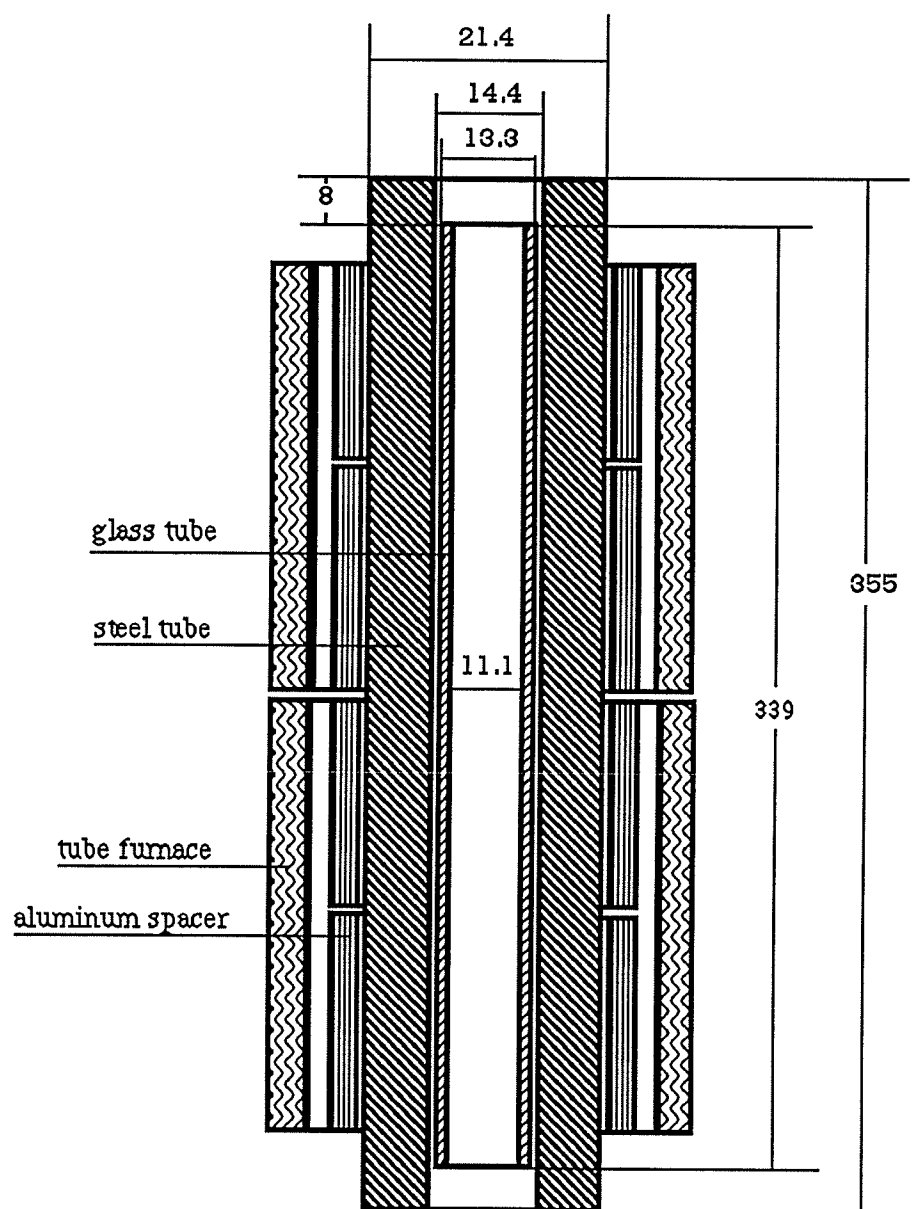


Figure 2.2-3. Steel reactor (Reactor I) (dimensions in mm)

(b). Two ozone generation methods (spark method and silent discharge method) were used in this reaction system.

(c) Input line

Two separate lines were constructed from 1/8" SS fittings and tubings (except for the connections of the silent discharge ozone generator which were connected by silicon rubber tubings) to control the pressure and flow rate of methane and oxygen gas. Methane and oxygen were supplied from the conventional high pressure cylinders (Linde Union Carbide). The delivery pressure of each gas was controlled at 60 psig with a reducing regulator fitted with a shut-off valve.

The flow rates of  $O_2$  and  $CH_4$  were monitored and controlled by two mass flow controller (BROOKS 5850D). Both  $O_2$  and  $CH_4$  were filtered through 7 micron NUPRO "F" series compact in-line filter installed prior to the mass flow controller in each line to protect the mass flow controller. In the  $O_2$  line, an IDEAL AEROSMITH needle valve with vernier adjustment (V 54-2-11) was inserted prior to the NUPRO filter to provide the fine control required to set the small  $O_2$  flow rate.

Following the mass flow controller each line was equipped with a VALIDYNE DP 15 Pressure Transducer (0-85 atm. diaphragm for the  $CH_4$  or  $C_2H_6$  line and 0-34 atm. diaphragm for the  $O_2$  line) operating at integral mode to monitor and measure the absolute pressure of the feed-gas in the system. Another VALIDYNE DP 15 Pressure Transducer (0-136 atm. diaphragm) was installed on the six-port SS block which was situated just above the reactor to measure the pressure of reaction in the reactor. The output from the transducer was read directly from a VALIDYNE Four Channel Digital Indicator (model CD 280-4RM). Each channel was set to zero prior to calibration.

The check-valve in each line just prior to the mixing cross prevented the backflow of the gases of the line.

Pure  $O_2$  gas was partially converted to ozone in the ozone generator. The gas mixture of  $O_2$  and  $O_3$  met with  $CH_4$  in the mixing cross before passing into the reactor.



The mixing cross was filled with Teflon turnings to reduce the dead volume and increase turbulence.

A vernier needle valve (IDEAL AEROSMITH V 54-2-11) was inserted into the input line following the mixing cross to further provide turbulence to improve the mixing quality.

A six-port SS block was installed just above the reactor to provide the connection ports. They were connected to the input gas line, the reactor, the relief valve, the pressure transducer and the thermocouple probe, respectively. The one remaining port was stoppered and it could be used to connect the pure  $N_2$  gas which was used to purge the reactor or directly connected to the ozone generator to shorten the distance between the ozone generator and the reactor.

A line carrying pure nitrogen gas from a supply cylinder was connected into the system via a three-way valve prior to the 7 micron filter in the  $CH_4$  line to substitute  $N_2$  for  $CH_4$  at the beginning of operation of the reaction and purge the reactor after the reaction.

#### (d) Output line

The output line was made from 316 stainless steel tubing in the hot section and from rubber tubing in the cold section. A 300 mm  $\times$  1/8" o. d. length of SS tubing was connected between the reactor and the sampling port with silicon rubber seal. To prevent condensation of products, the 300 mm long SS tubing was heated by electrothermal tapes and the sampling port was heated by a cylindrical heating element. The heating tape and the heating element were insulated to effect a high temperature. Both the temperature of this line and the temperature of the sampling port were controlled with two Variacs at about 120 °C and monitored by two Chromel-Alumel thermocouple probes with 1/16" 304 SS sheath whose outputs were connected via a selection switch to a OMEGA Temperature Controller (model CN 300 KC) acting only as a temperature indicator. The temperatures were directly read from this controller alternatively.

The cold section between the sampling port and the soap bubble flowmeter was connected with rubber tubing.

The flow rate of the output gas was measured with a soap bubble flowmeter and then converted to values at S.T.P.

(e) Analysis section

The products were sampled with a 1 mL HAMILTON hot syringe (at 326 °K). The hot sample gas was quickly injected via the injection port into a HEWLETT PACKARD 5710A Gas Chromatograph or a FISHER-HAMILTON Gas Partitioner with the sample size of 0.6 mL. The permanent gases ( $N_2$ ,  $O_2$ , CO) were analyzed by the FISHER-HAMILTON Gas Partitioner and the other components of the sample were analyzed by the HEWLETT PACKARD Gas Chromatograph. The results of analysis of both G.C.s were processed and plotted by a PERKIN-ELMER SIGMA 10 DATA SYSTEM. The columns and the operation conditions of both G.C.s were the same as those of the reaction system with the glass reactor III which will be explained later in this chapter.

Experimental procedure

First, the shut-off valves [7], [8], [9], [14] and [15] were closed, the three pressure regulators [4], [5], and [6] were turned to fully closed and the three-way valve [11] were turned to the  $N_2$  line. Then, both of the two mass flow controller [16] and [17] were switched on and allowed to stabilize for 15 minutes before charging any gases.

The VALIDYNE Digital Indicator was turned on. The oxygen cylinder was opened and the delivery pressure of  $O_2$  was slowly increased to 60 psig by adjusting the regulator [4]. The vernier valve [10] was opened approximately 2 turns. The shut-off valves [7] and [14] were slowly opened to allow  $O_2$  to be admitted into the system. The mass flow controller was set to 20 mL/min. according to the predetermined calibration curve of the mass flow controller. This flow rate was kept for 10 min. for the spark ozone generator

and 30 min. for the silent discharge generator to permit  $O_2$  to replace the air in the line between the  $O_2$  cylinder and the mixing cross.

The flow rate of  $O_2$  was reduced to the desired value (usually less than 3 mL/min) by adjusting both the vernier needle valve [10] and the mass flow controller [16]. The  $N_2$  cylinder [3] was opened and, after the  $N_2$  pressure was reduced to 60 psig by the regulator [6], the shut-off valves [9] and [15] were slowly opened and  $N_2$  instead of  $CH_4$  was admitted into the system to prevent the possible explosion caused by exceeding the explosion limit of the mixture of  $CH_4$  and  $O_2$ . The flow rate of  $N_2$  was set to the same as that of  $CH_4$  to be admitted later according to the predetermined calibration curve. The total flow rate of the gas mixture was measured with the soap bubble flowmeter [31]. When both flow rate of  $N_2$  and  $O_2$  were stable, the  $CH_4$  cylinder was opened and the delivery pressure of the  $CH_4$  was adjusted to 60 psig by the regulator [5] and the shut-off valve [8] was opened. The three-way valve [11] was turned to the  $CH_4$  line, and  $CH_4$  was substituted for  $N_2$  and introduced into the system.

The crude composition of the feedstock was estimated by the flow rate settings of the two mass flow controllers. The accurate composition of input gas was sampled at the sampling port in the output line after charging  $CH_4$  for 75 minutes.

The ozone generator was started, both of the two temperature controllers were set to the desired temperatures, and the heaters for the reactor were turned on. The Variac for the pre-reaction heater was slowly increased to 80 V (reading on the Variac) and the Variac for the reaction heater set to 100 V (reading on the Variac). At the same time, the output line and the sampling port was heated and the temperatures were slowly increased to the 120 °C by adjusting the two Variacs. It usually took 1 hour for the temperatures to reach the desired values.

After the composition of output gas was stable (about 2.5 hours for the spark ozone generator and 4.5 hours for the silent discharge ozone generators), analysis of the products

was begun. Each determination took about 1 hour and at least two determinations were made for each run of the reaction studied.

At the end of the experiment, all the heaters were turned off, the O<sub>2</sub> cylinder was closed, the shut-off valves [7] and [14] were closed, and the CH<sub>4</sub> cylinder was closed. The three-way valve was switched to N<sub>2</sub> line and nitrogen gas was admitted to purge the system. After purging, the N<sub>2</sub> cylinder [3] was closed and the valves [9] and [15] were closed. All of the electrical instruments were switched off.

#### **2.2.2. The reaction system with a Pyrex glass reactor (Reactor II) (referred to as System II)**

This reaction system is shown schematically in Figure 2.2-4. From the three high-pressure supply cylinders to the two mass flow controllers, i.e., from [1] to [17], System I and System II were identical.

A VALIDYNE DP 15 Pressure Transducer with a 0-34 atm. diaphragm was used to monitor the pressure in the ozone generator. The output of this transducer was directly read from the VALIDYNE Digital Indicator (model CD 280-4RM).

The ozone generator [19] was a single Pyrex glass Berthelot ozonizer<sup>39</sup> (63.5 cm long) (Figure 2.1-3b).

The check-valve [20] was used to prevent the backflow of other gases into the ozone generator thus influencing the operation of the generator.

The mixing tube [21] was a 180 mm x 20 mm o.d. Pyrex glass tube which was filled with 4 mm diameter glass beads to reduce the dead volume and increase turbulence to improve the mixing quality.

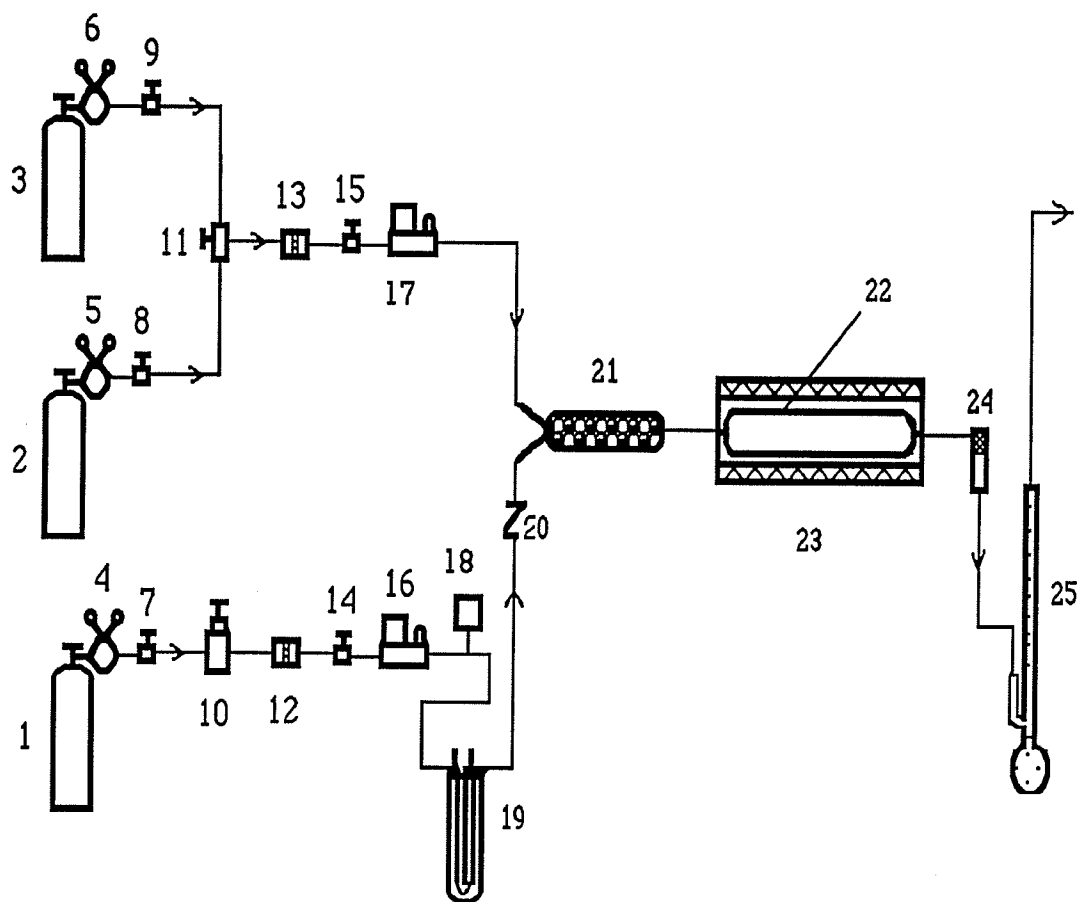


Figure 2.2-4. The reaction system with a Pyrex glass reactor (Reactor II)

- |                                    |                             |
|------------------------------------|-----------------------------|
| 1. O <sub>2</sub> cylinder         | 2. CH <sub>4</sub> cylinder |
| 3. N <sub>2</sub> cylinder         | 4, 5, & 6. regulators       |
| 7, 8, 9, 14, & 15. shut-off valves | 10. vernier needle valve    |
| 11. three-way valve                | 12 & 13. filters            |
| 16 & 17. mass flow controllers     | 18. pressure transducers    |
| 19. ozone generator                | 20. check-valve             |
| 21. mixing tube                    | 22. reactor                 |
| 23. furnace                        | 24. sampling port           |
| 25. soap bubble flowmeter          |                             |

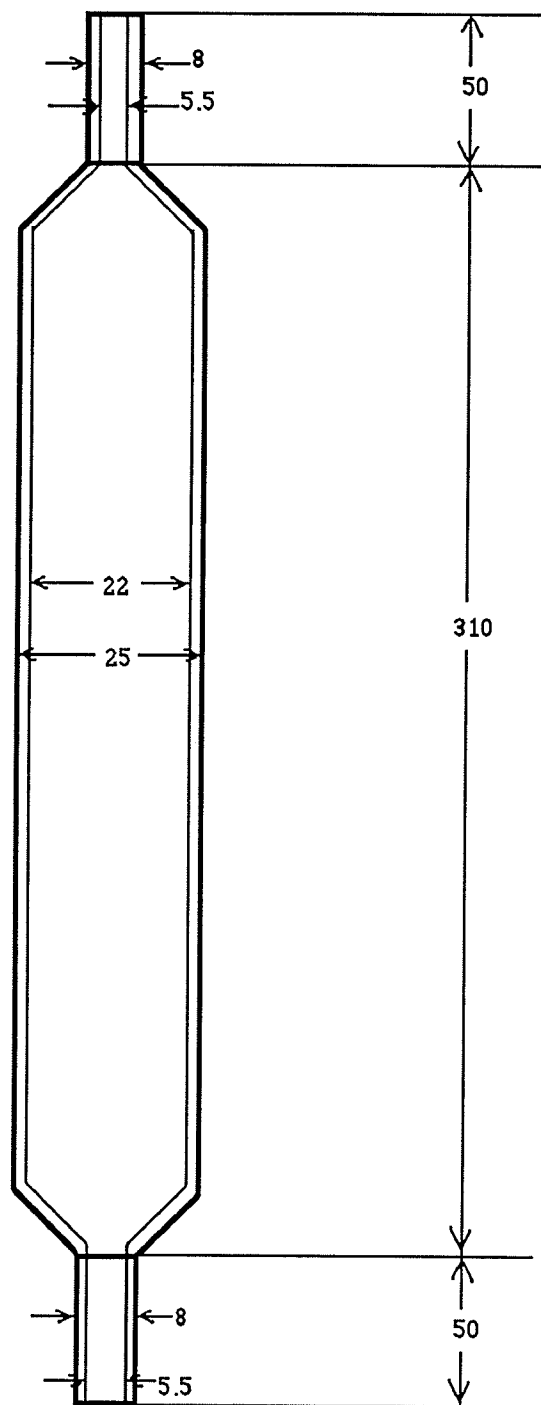


Figure 2.2-5. Pyrex glass reactor (Reactor II) (dimensions in mm)

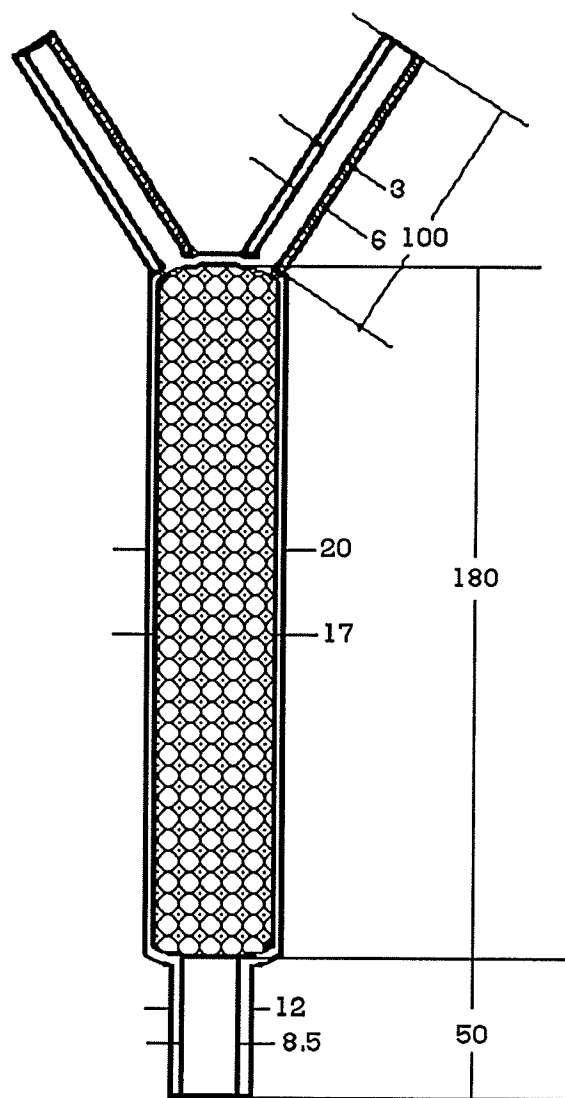


Figure 2.2-6. Glass bead mixing tube I (dimensions in mm)

The reactor, made from Pyrex glass and having a volume of 120.7 mL (dimension shown in Figure 2.2-5), was placed horizontally in a LINDBERG Furnace which was controlled by a OMEGA Temperature Controller (model CN 300 KC). The hot junction of a subminiature quick disconnect Chromel-Alumel thermocouple probe with 0.02" 304 SS sheath (OMEGA ENG INC) was fastened on the middle outside wall of the reactor to monitor and measure the reaction temperature. The cold ends were connected to the temperature controller. The temperature was read directly from the display of the temperature controllers.

The 15 cm long output line between the reactor and the sampling port with silicon rubber seal was constructed from 8 mm o.d. Pyrex glass tubing. This section of the line was heated to 120 °C (to prevent condensation of the high boiling point products) by a cylindrical heater which was controlled by an OMEGA Temperature Controller (model CN 300 KC) and a 1/16" 304 SS sheath Chromel-Alumel thermocouple probe. The sampling port was also heated to 120 °C by another cylindrical heater which was controlled by a Variac and another OMEGA 1/16" Chromel-Alumel thermocouple probe whose output was read from the third temperature controller (OMEGA CN 300 KC) acting as a temperature indicator. The two heaters and sampling port were insulated with asbestos cloth and glass wool.

The flow rate of the output gas was measured with a soap bubble flowmeter.

The analysis method of this system was the same as that of System I. The lines between supply cylinders and the mass flow controllers were constructed from 1/8" 316 stainless steel tubing. The lines between the ozone generator [19], the mixing tube [21], the reactor [22], and the sampling port [24] was connected with 8 mm Pyrex glass tubing and short lengths of silicon rubber tubing.



### Experimental procedure

The experimental procedure was the same as that of System I except that only silent discharge generator was used to convert part of the  $O_2$  to  $O_3$ .

#### **2.2.3. The reaction system with a modified Pyrex glass reactor (Reactor III) (referred to as System III)**

Compared to System II (Figure 2.2-4), five modifications were made for this reaction system (Figure 2.2-7).

##### **(a). mixing tube**

In order to reduce the dead volume, the size of the mixing tube was reduced in this reaction system, as shown in Figure 2.2-8. The smaller Pyrex glass beads (1.5 ~ 2 mm diameter) was used to fill this mixing tube.

##### **(b). ozone generator**

Ozone generator was the double Pyrex glass Berthelot silent discharge ozonizers<sup>39</sup> (54.5 cm and 63.5 cm long) (Figure 2.1-3b) as shown in Figure 2.1-3a

##### **(c). reactor**

The new reactor (Reactor III) was made from the same material as the old one (Reactor II) but the shape and the dimensions, as shown in Figure 2.2-9, were different from the old one. In order to get more accurate reaction temperatures, the thermocouple probe was inserted into the center of the reactor through a 4 mm o.d. Pyrex glass tube (with one end sealed) which was fixed in the reactor. The position of the hot junction of the thermocouple probe could be easily changed. The reactor was made to be 5 cm shorter than the heating furnace in order to ensure that the temperature at the entrance of the reactor was close to the reaction temperature. The entrance tubing (9 cm long) of the reactor was made from 1 mm i.d. Pyrex capillary glass tubing in order to decrease the residence time of  $O_3$  outside the reactor.

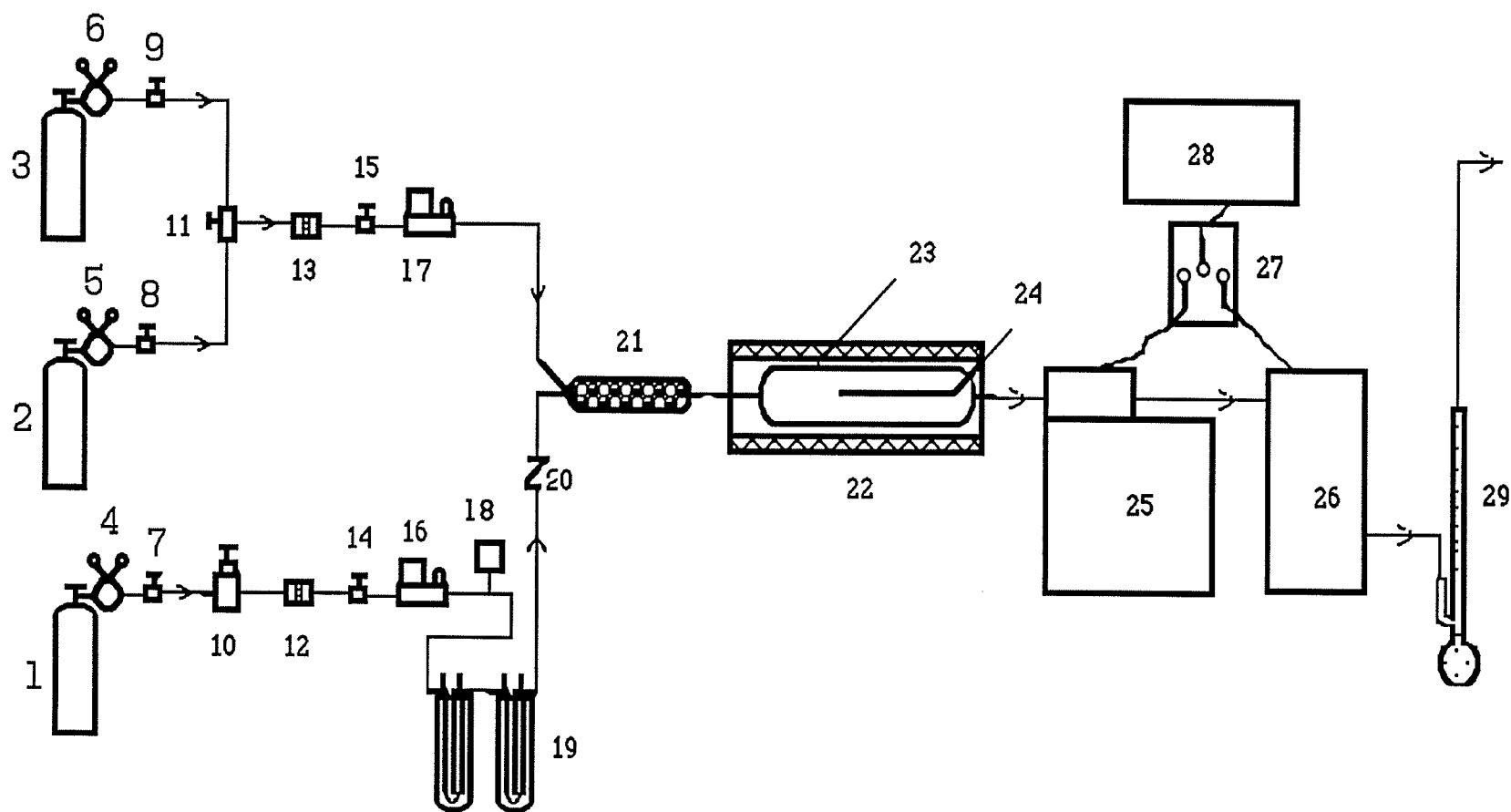


Figure 2.2-7. The reaction system with a modified glass reactor (Reactor III)

Figure 2.2-7. The reaction system with a modified Pyrex glass reactor (Reactor III)

- |                                |   |
|--------------------------------|---|
| 1. O <sub>2</sub> cylinder     | 2. CH <sub>4</sub> (or C <sub>2</sub> H <sub>6</sub> ) cylinder |
| 3. N <sub>2</sub> cylinder     | 4, 5,&6. regulators   |
| 7, 8,9,14,&15. shut-off valves | 10. vernier needle valve  |
| 11. three-way valve            | 12 &13. filters   |
| 16 &17. mass flow controllers  | 18. pressure transducer   |
| 19. ozone generators           | 20. check-valve   |
| 21. mixing tube                | 22 furnace  |
| 23. reactor                    | 24. thermocouple probe  |
| 25. gas chromatograph          | 26. gas partitioner   |
| 27. selection switch           | 28. Sigma data system   |
| 29. soap bubble flowmeter      |   |

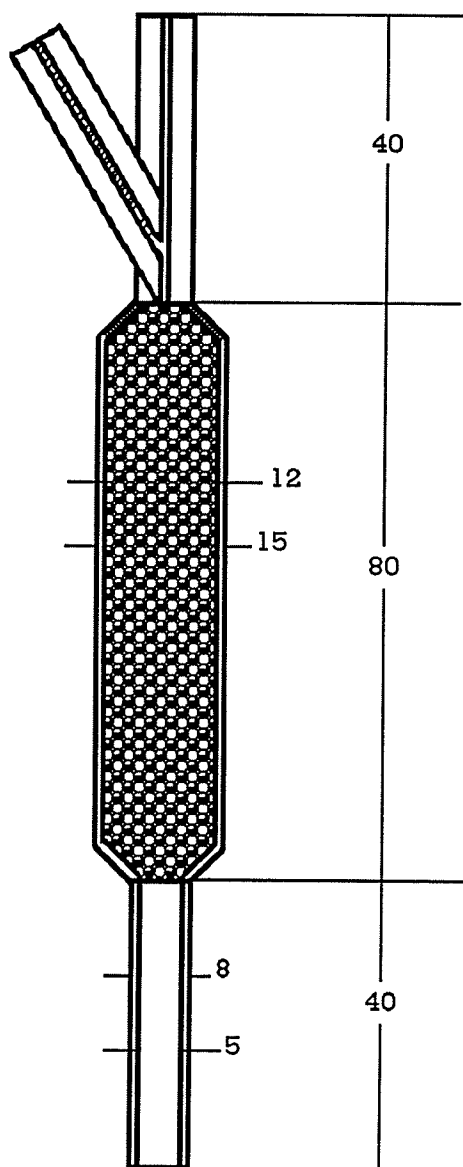


Figure 2.2-8. Glass bead mixing tube II (dimensions in mm)

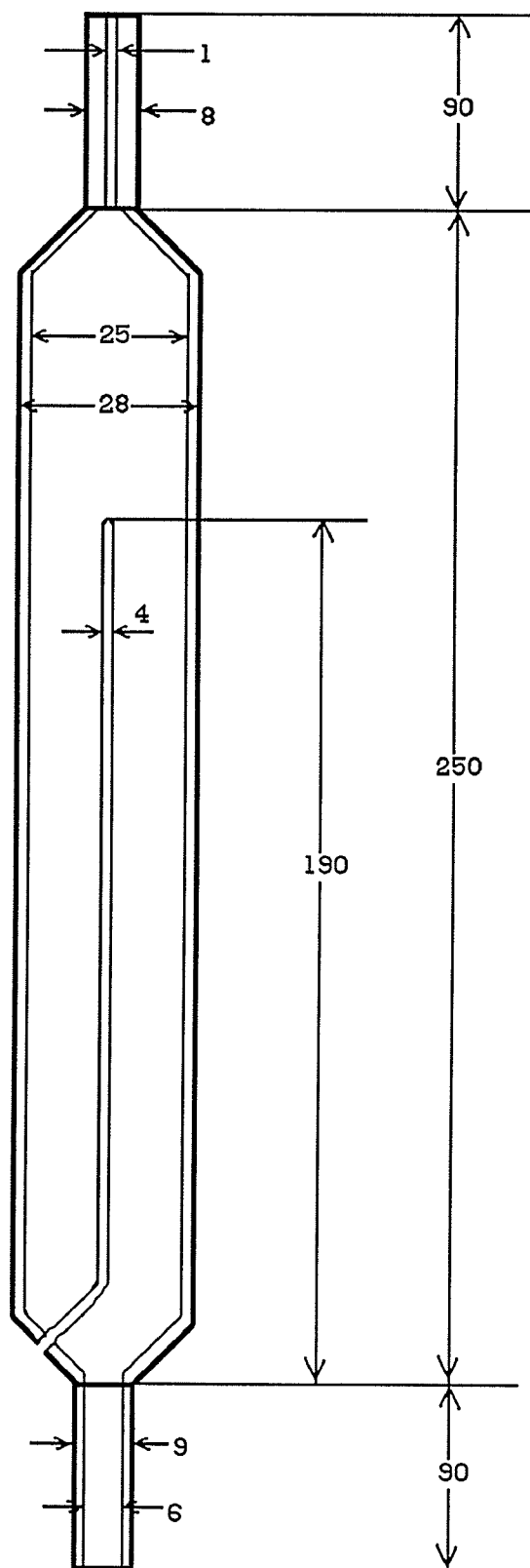


Figure 2.2-9. Modified glass reactor (Reactor III) (dimensions in mm)

(d). capillary tubing for connection

Pyrex capillary glass tubing with 1.5 mm i.d. (8 mm o.d.) was used to construct the line between the exit of the ozone generators and the reactor to reduce the dead volume.

(e). on-line analysis

Because the conversion of the  $\text{CH}_4$  (or  $\text{C}_2\text{H}_6$ ) was low, it was difficult to do quantitative analysis and mass balance determination by the syringe sampling method so an on-line analysis was developed in System III.

The output line (65 cm long) between the reactor and HEWLETT PACKARD 5710A Gas Chromatograph was constructed from 1/8" 316 SS tubing. This section of the line was heated by one cylindrical heater (near the reactor) and two electrothermal tapes to 115 ~ 120 °C to prevent the condensation of products with higher boiling points. The cylindrical heater was controlled by an OMEGA Temperature Controller (model CN 300 KC) and the electrothermal tapes by a Variac. Three Chromel-Alumel thermocouple probes (OMEGA ENG. INC.) with 1/16" 304 SS sheath were used to monitor the temperatures in this section of the line. The outputs of two of the three thermocouple probes were connected via a selection switch to an OMEGA Temperature Controller (model CN300 KC) acting as a temperature indicator. The temperatures were read directly from the display.

A SEISCOR MODEL VIII high pressure, high temperature valve, having a sample volume of 0.6 mL, was used to sample the product gas for the HEWLETT PACKARD Gas Chromatograph throughout the study. It was situated in the thermostat on the top of the G.C. and was kept at 115 °C to prevent condensation in the valve. This pneumatically actuated diaphragm valve with a total switching time of about 10 milliseconds was capable of introducing accurately and repeatedly samples into the carrier gas stream. The cylinder air, filtered through a 7 micron NUPRO "F" series compact in-line filter, was used as the actuating gas in all the experiments.

The product gas, having passed through the SEISCOR sampling valve, was sampled by the sampling valve (with sample size 0.6 mL) in the FISHER-HAMILTON Gas Partitioner, and then passed through the soap bubble flowmeter to the vent.

#### Experimental procedure

The experimental procedure was the same as that of System II except for requirement of 40 minutes longer time for obtaining constant concentration of the products and that the products were sampled with the sampling valves instead with the syringe.

#### **2.2.4. Analysis System**

Based upon the experiences of the previous research staff of this laboratory, a  $10' \times 1/8"$  o.d. 316 stainless steel column packed with HayeSep D (80-100 mesh) was used in a HEWLETT PACKARD 5710A Gas Chromatograph (referred to as HP G.C.). The separation between CO, CO<sub>2</sub>, H<sub>2</sub>O, HCHO, CH<sub>3</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>OH and other hydrocarbons (C<sub>2</sub> and C<sub>3</sub>) was found to be quite satisfactory in this column under the column temperature program.

However, this column was unable to separate N<sub>2</sub>, O<sub>2</sub> and CO at room temperature. Three means were tried to improve the separation of these compounds but all were unsuccessful. The first of these was to cool the column temperature to -30 °C using dry ice. Although the separation of CO from N<sub>2</sub> and O<sub>2</sub> was excellent, the resolution of O<sub>2</sub> and N<sub>2</sub> was very poor. The second was to reduce the column temperature further to about -180 °C using a liquid N<sub>2</sub> trap. It was possible to separate O<sub>2</sub> from N<sub>2</sub>, but a split-peak for C<sub>2</sub>H<sub>6</sub> was observed. The third method was to use two different columns in series. A Carbosieve SII (100-120 mesh) column ( $2' \times 1/8"$  316 SS) was followed by a  $10' \times 1/8"$  316 SS column packed with HayeSep D (80-100 mesh). Although the separation between

the gases was improved in this arrangement, long tailing for different components was observed. Hence, this combination was unsuitable for analysis in the study.

The separation between  $O_2$ ,  $N_2$  and CO was successfully carried out at room temperature ( $\sim 21^\circ C$ ) in a  $6.5' \times 1/8''$  SS column packed with Molecular Sieve 13X (40-60 mesh) installed in a FISHER-HAMILTON Gas Partitioner (referred to as F-H G.P.). In the F-H G.P., two columns were in series. A  $6' \times 1/4''$  aluminum column packed with 30% DEHS on 60-80 mesh Chromosorb P was followed by the MS 13X column. The separation between  $N_2$ ,  $O_2$ ,  $CH_4$ , CO, and  $C_2H_6$  was good.

The analysis of the reactants and products, therefore, was carried out by the combination of the HP G.C. and F-H G.P. throughout this study.

Helium was used as the carrier gas and a SERVOMEX Thermoconductivity detector (HP G.C.) and a F-H Model 29 Thermoconductivity detector (F-H G.P.) were used for detection. The first thermoconductivity detector was controlled by a SERVOMEX Katharometer Control Unit and the second thermoconductivity detector was controlled by the F-H G.P. itself.

The outputs of the two thermoconductivity detectors were connected to a PERKIN-ELMER Sigma 10 Data system via a selection switch. The results of the analysis from the HP G.C. and from the F-H G.P. were obtained directly from the Data system alternatively.

The flow chart for the the feed-gas, products and the carrier gas in this analysis system is shown in Figure 2.2-10.

The operation parameters for the HP G.C. and for the F-H G.P. as well as the programs for the PERKIN-ELMER Sigma 10 Data System are given in Appendix A.



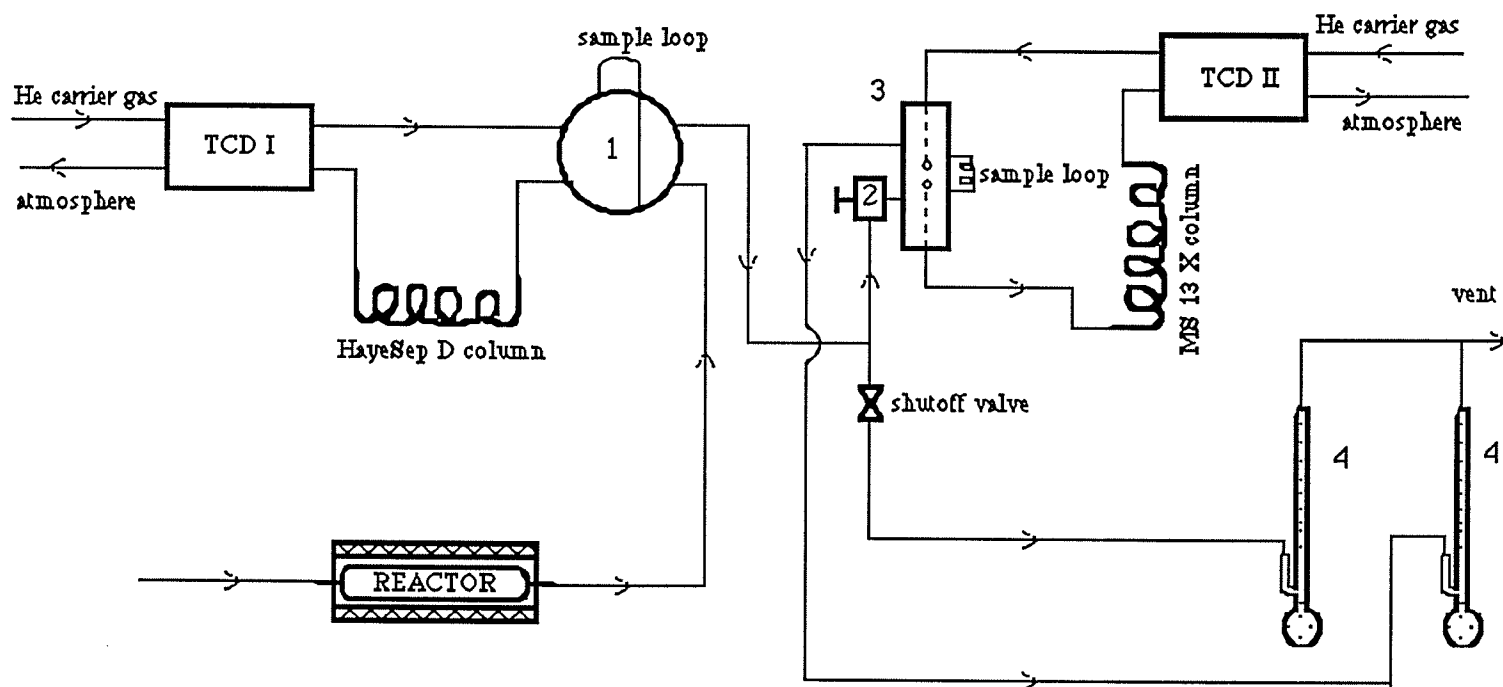


Figure 2.2-10 Flow chart of the feed-gas and products in the analysis system

1. Seiscor VIII Sampling Valve

2. Three-way valve

3. F-H Sampling Valve

4. Soap bubble flowmeter

TCD I SERVOMEX Thermoconductivity Detector

TCD II F-H Thermoconductivity Detector

### 2.2.4.1. Calibration of HP G.C. and F-H G.P.

#### (i) F-H G.P. Relative Response Factor (RRF) Determination

The relative response factors for the F-H G.P. were determined as follows.

For O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, a fixed volume (0.600mL), constant temperature and pressure sample loop on the F-H G.P. was used to inject each pure compound, respectively, into the F-H G.P. at an outlet pressure of one atmosphere to determine the response area for each compound. Three determinations for each compound were made to obtain an average response value and the precision for each compound. The influence of the impurity in each compound gas and the change, if any, in temperature or pressure in the sample loop on the response value was corrected. The relative response factor was determined relative to methane. Thus, the relative response factor for methane is 1.000 by definition.

$$RF_i = \frac{A_i}{n_i} ,$$

where RF is Response Factor, n is the moles of a compound, and A is Response Area value. For example,

$$RF_{CH_4} = \frac{A_{CH_4}}{n_{CH_4}}$$

$$\text{Since } n_i = \frac{P_i V_i}{RT_i}, \quad n_{CH_4} = \frac{P_{CH_4} V_{CH_4}}{RT_{CH_4}}$$

$$P_i = P_{CH_4}, \quad V_i = V_{CH_4}, \quad \text{and} \quad T_i = T_{CH_4}$$

$$\text{Therefore } n_i = n_{CH_4}$$

Hence

$$RRF_i = \frac{RF_i}{RF_{CH_4}} = \frac{A_i}{A_{CH_4}}$$

where  $RRF_i$  is the Relative Response Factor for compound i.

Instead of pure carbon monoxide, a standard gas mixture of CO, CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, prepared by P. C. Das, was injected by the above-mentioned sample loop into F-H G.P. to determine the response value for carbon monoxide. Three determinations were made to obtain the average value and the precision of F-H G.P. The relative response factor of CO relative to CH<sub>4</sub> was calculated as follows

$$\frac{y_{\text{CO}}}{y_{\text{CH}_4}} = \frac{\left[ \frac{A_{\text{CO}}}{\text{RRF}_{\text{CO}}} \right] / \sum \frac{A_i}{\text{RRF}_i}}{\left[ \frac{A_{\text{CH}_4}}{\text{RRF}_{\text{CH}_4}} \right] / \sum \frac{A_i}{\text{RRF}_i}} = \frac{\frac{A_{\text{CO}}}{\text{RRF}_{\text{CO}}}}{\frac{A_{\text{CH}_4}}{\text{RRF}_{\text{CH}_4}}} = \frac{A_{\text{CO}}}{A_{\text{CH}_4}} \times \frac{\text{RRF}_{\text{CH}_4}}{\text{RRF}_{\text{CO}}}$$

$$\frac{\text{RRF}_{\text{CO}}}{\text{RRF}_{\text{CH}_4}} = \frac{A_{\text{CO}}}{A_{\text{CH}_4}} \times \frac{y_{\text{CH}_4}}{y_{\text{CO}}}$$

where y is the mole fraction of a compound in the gas mixture.

The standard gas mixture was prepared by Das from pure gases with a Seederer-Kohlbusch balance (sensitivity 15 mg) and the concentrations of the components in it are given in Table 2.2-1. The relative response factors are given in Table 2.2-2 and the literature values are given in Appendix D. The linearity of the thermoconductivity of F-H G.P. was checked by injecting different volumes of air into the F-H G.P. with a 1 mL HAMILTON Syringe to determine the response area for O<sub>2</sub> and N<sub>2</sub>. The linearity was very good (the average correlation coefficient = 0.99980) as shown in Figure 2.2-11.

Table 2.2-1. The composition of the standard gas mixture

Compound	Concentration (mol %)
CH <sub>4</sub>	85.28 ± 0.86
C <sub>2</sub> H <sub>6</sub>	1.74 ± 0.16
CO	8.32 ± 0.21
CO <sub>2</sub>	4.65 ± 0.13

Table 2.2-2. F-H G.P. Relative Response Factors (RRF)

Compound	RRF	$\frac{\sigma}{\text{RRF}}$
CH <sub>4</sub>	1.000	
N <sub>2</sub>	1.145 ± 0.004	0.003
O <sub>2</sub>	1.130 ± 0.001	0.0009
CO	1.28 ± 0.08	0.06
C <sub>2</sub> H <sub>6</sub>	1.525 ± 0.007	0.005

σ standard deviation

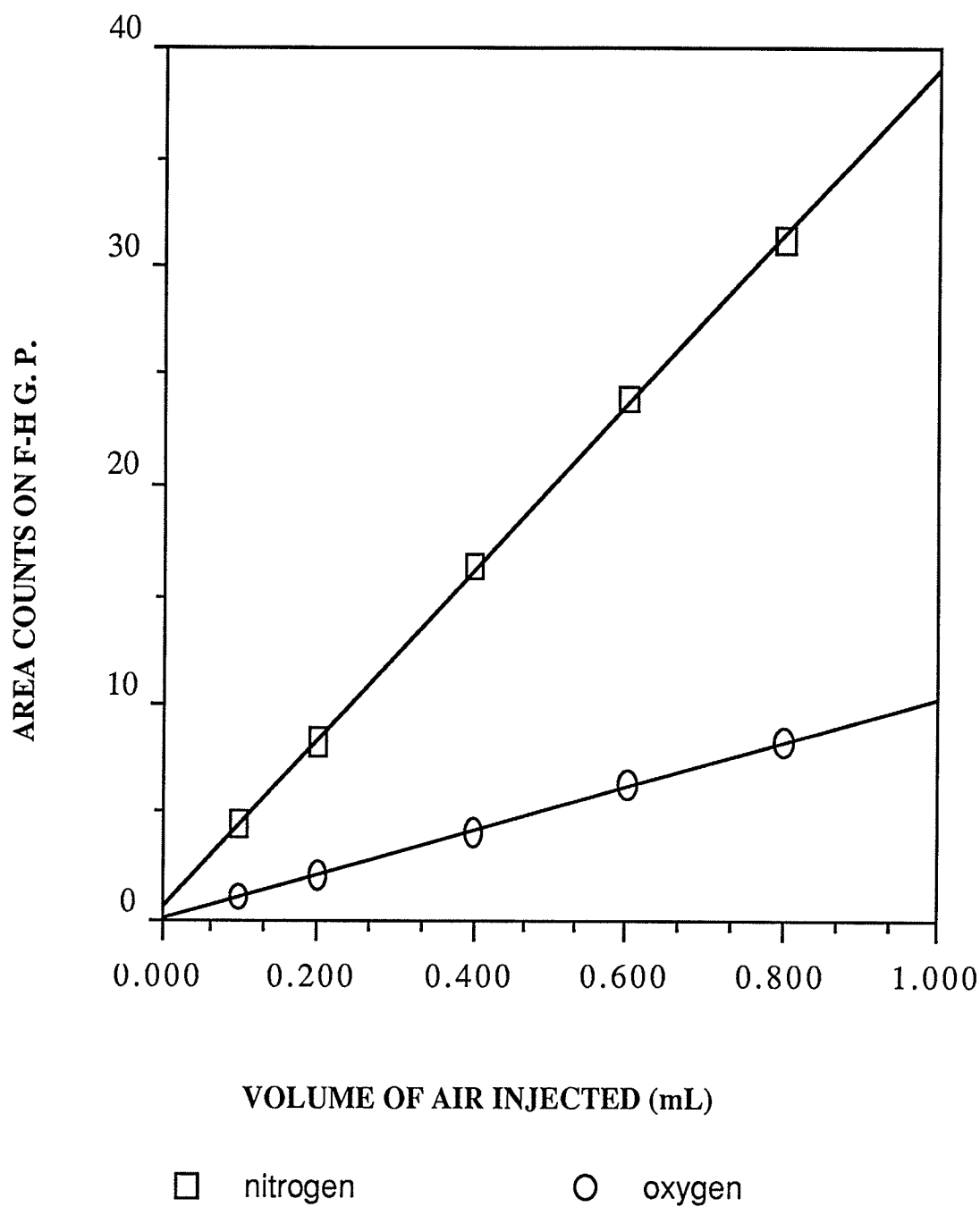


Figure 2.2-11. Plot of the response area counts of  $O_2$  and  $N_2$  in air vs sample size on F-H G.P.

## (ii) H-P G.C. Relative Response Factor Determination

### (a). gaseous compounds

For  $O_2$ ,  $N_2$ ,  $CH_4$ , and  $C_2H_6$ , the relative response factors were determined by using pure samples of the each compound, a fixed sample loop on the SEISCOR VIII Sampling Valve and the same method as described in the determination of the RRFs of these gases for F-H G.P.

The standard gas mixture prepared by Das, the fixed sample loop and the same method as that for the determination of  $RRF_{CO}$  on F-H G.P. were used to determine the RRFs for  $CO$ , and  $CO_2$ .

Since only trace amount of ethylene was found in the product gas, the RRF of this compound was not calibrated directly. The ratio of  $RRF_{C_2H_4}$  to  $RRF_{C_2H_6}$  was taken from the literature<sup>40</sup> (0.985). The linearity of the HP G.C. was also checked by injecting different sample volumes of air in this G.C. with the 1 mL HAMILTON Syringe. The correlation coefficient was found to be 0.999908. The plot is shown in Figure 2.2-12.

### (b) liquid compounds

For  $H_2O$ ,  $CH_3OH$ , and  $CH_3CH_2OH$ , pure compounds were used to determine the response factor by injecting different volumes of the liquid compound into the injection port of the HP G.C. with a 1  $\mu$ L HAMILTON Syringe. At least three determinations were made for each sample size in order to calculate an average response value and the analysis precision. The response factor was obtained by plotting response value vs sample size and through the calculation as follows

$$RF_i = \frac{A_i}{n_i}, \quad n_i = \frac{V_i \rho_i}{M_i}$$

$$RF_i = \frac{A_i M_i}{V_i \rho_i},$$

where A is the response area counts corresponded to 1  $\mu\text{L}$  injection obtained from the plot,  $\rho$  is the density of the compound ( $\text{g} / \text{mL}$ ) and M is the molar mass of the compound ( $\text{g} / \text{mol}$ ).

The compounds used for calibration were specified as follows:

$\text{H}_2\text{O}$	double distilled
$\text{CH}_3\text{OH}$	99.9%, Analytical Reagent (A. R.), Fisher Scientific
$\text{C}_2\text{H}_5\text{OH}$	100%, Can. Ind. Alc. & Chem. Ltd

For  $\text{HCHO}$ , a liquid mixture of 37.1 (wt)% formaldehyde analytical reagent from Fisher Scientific was re-analyzed by the method of Seyewetz, Gibello and Sadtler<sup>41</sup> using 0.1% thymolphthalein as an indicator. Three determinations were made to get an average value and analysis precision. It was found that the concentration of formaldehyde in the mixture was  $36.02 \pm 0.06$  (wt) %. A standard liquid mixture of  $12.87 \pm 0.02$  (wt) %, prepared using a Fisher Scientific Mettler analytical balance by adding distilled water, was used to determine the response factor of formaldehyde. Three different sample volumes (0.200  $\mu\text{L}$ , 0.400  $\mu\text{L}$  and 0.600  $\mu\text{L}$ ) were injected with the 1  $\mu\text{L}$  HAMILTON Syringe. At least three determinations were made for each sample size in order to calculate an average value and analysis precision. The response area vs sample size was plotted.

$$\text{RF}_{\text{HCHO}} = \frac{A_{\text{HCHO}}}{n_{\text{HCHO}}} = \frac{A_{\text{HCHO}}}{V_{\text{mix}} \rho_{\text{mix}} \times 12.87\% / M_{\text{HCHO}}} = \frac{A_{\text{HCHO}} M_{\text{HCHO}}}{V_{\text{mix}} \rho_{\text{mix}} \times 12.87\%}$$

For  $\text{CH}_3\text{CHO}$ , a liquid mixture of  $\text{CH}_3\text{CHO}$  (1) from BDH Chemicals Ltd (not less than 99%) and double distilled  $\text{H}_2\text{O}$  (2) with  $n_1/n_2 = 0.1123$ , prepared using the Fisher Scientific Mettler analytical balance, was used to determine the response factor of acetaldehyde by injecting different sample volumes (0.100  $\mu\text{L}$ , 0.200  $\mu\text{L}$ , 0.300  $\mu\text{L}$ , and 0.400  $\mu\text{L}$ )

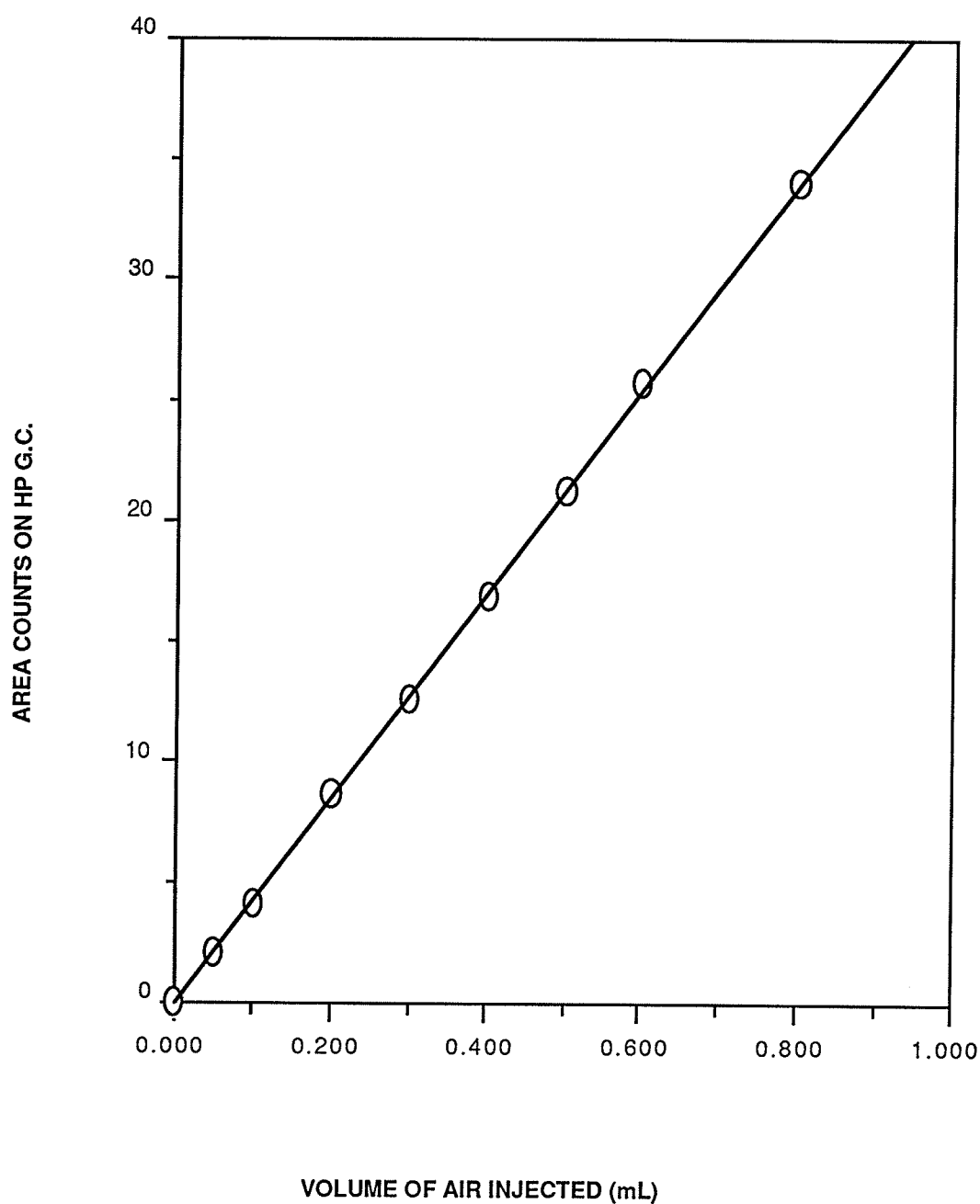


Figure 2.2-12. Plot of the response area counts of air vs sample size on the HP G.C.



of the liquid mixture into the injection port with the 1  $\mu\text{L}$  HAMILTON Syringe. Seven determinations were made to calculate an average response value and the precision of the analysis.

$$\frac{\text{RRF}_{\text{CH}_3\text{CHO}}}{\text{RRF}_{\text{H}_2\text{O}}} = \frac{A_{\text{CH}_3\text{CHO}}}{A_{\text{H}_2\text{O}}} \times \frac{x_{\text{H}_2\text{O}}}{x_{\text{CH}_3\text{CHO}}} = \frac{A_{\text{CH}_3\text{CHO}}}{A_{\text{H}_2\text{O}}} \times \frac{1}{0.1123}$$

where  $x$  is the mole fraction of the compound.

In order to calculate the relative response factors (relative to methane) of the liquid compounds, pure  $\text{CH}_4$  was used to determine the mole response factor of methane by injecting three different sizes of methane into the injection port of the HP G.C. with the 1 mL HAMILTON Syringe. Three determination were made for each sample size to obtain an average value and analysis precision. The impurity in methane was taken into account. The response factor was calculated from the following equation,

$$\text{RF}_{\text{CH}_4} = \frac{A_{\text{CH}_4}}{n_{\text{CH}_4}} = \frac{A_{\text{CH}_4}}{P_{\text{CH}_4} V_{\text{CH}_4} / R T_{\text{CH}_4}} .$$

The calibration by the syringe injection was related to the calibration by the sample valve by the value of  $\text{RF}_{\text{CH}_4}$  on the HP G.C.

Thus, the RRFs of the liquid compounds were calculated by the equation,

$$\text{RRF}_i = \frac{\text{RF}_i}{\text{RF}_{\text{CH}_4}}$$

All the relative response factors obtained for the HP G.C. are given in Table 4 and the literature values are given in Appendix D.

### 2.2.4.2 Determination of the Composition of the Feed-gas and the Product Gas.

#### (a) feed-gas

The composition of the feed-gas was determined using only the F-H G.P. for methane partial oxidation and the HP G.C. for the ethane partial oxidation. The equations for the calculation of the composition was derived as follows.

Since

$$RF_i = \frac{A_i}{n_i} \quad \text{and} \quad n_i = \frac{A_i}{RF_i} \quad ,$$

so,

$$y_i = \frac{n_i}{\sum n_j} = \frac{A_i / RF_i}{\sum (A_j / RF_j)} = \frac{A_i / (RF_i / RF_{CH_4})}{\sum [A_j / (RF_j / RF_{CH_4})]} = \frac{A_i / RRF_i}{\sum (A_j / RRF_j)}$$

#### (b) product gas

Since  $O_2$ ,  $N_2$ , and  $CO$  were incapable of being efficiently separated by the HP G.C., and liquid (at room temperature) products could not be determined by the F-H G.P., the data from the F-H G.P. and from the HP G.C. were combined to determine the composition of the product gas by the following equations.

First, converting the data of  $O_2$ ,  $N_2$ , and  $CO$  obtained from F-H G.P. into the data for HP G.C.

$$\left[ \frac{n_j}{n_{CH_4}} \right]_{F-H} = \frac{\left[ \frac{A_j}{RF_j} \right]_{F-H}}{\left[ \frac{A_{CH_4}}{RF_{CH_4}} \right]_{F-H}} = \frac{\left[ \frac{A_j}{RF_j / RF_{CH_4}} \right]_{F-H}}{\left[ \frac{A_{CH_4}}{RF_{CH_4} / RF_{CH_4}} \right]_{F-H}} = \frac{\left[ \frac{A_j}{RRF_j} \right]_{F-H}}{\left[ \frac{A_{CH_4}}{A_{CH_4}} \right]_{F-H}} \quad ,$$

similarly,

$$\left[ \frac{n_j}{n_{CH_4}} \right]_{HP} = \frac{\left[ \frac{A_j}{RRF_j} \right]_{HP}}{\left[ \frac{A_{CH_4}}{RRF_{CH_4}} \right]_{HP}}$$

where the subscript F-H represents the values obtained from the F-H G. P., and the subscript HP from the HP G.C., respectively.

Since

$$\left[ \frac{n_j}{n_{CH_4}} \right]_{F-H} = \left[ \frac{n_j}{n_{CH_4}} \right]_{HP}$$

hence,

$$\left[ \frac{A_j}{RRF_j} \right]_{HP} = \left[ \frac{A_j}{RRF_j} \right]_{F-H} \times \frac{\left[ \frac{A_{CH_4}}{RRF_{CH_4}} \right]_{HP}}{\left[ \frac{A_{CH_4}}{RRF_{CH_4}} \right]_{F-H}}$$

consequently,

$$y_i = \frac{\left[ \frac{A_i}{RRF_i} \right]_{HP}}{\sum \left[ \frac{A_j}{RRF_j} \right]_{HP}}$$

Table 2.2-3. HP G.C. Relative Response Factors (RRF)

Compound	RRF	$\frac{\sigma}{\text{RRF}}$
N <sub>2</sub>	1.323 ± 0.014	0.011
O <sub>2</sub>	1.274 ± 0.013	0.010
CO	1.207 ± 0.045	0.037
CO <sub>2</sub>	1.56 ± 0.06	0.04
CH <sub>4</sub>	1.000	
C <sub>2</sub> H <sub>6</sub>	1.567 ± 0.014	0.0090
H <sub>2</sub> O	0.777 ± 0.015	0.019
HCHO	1.01 ± 0.02	0.02
CH <sub>3</sub> OH	1.70 ± 0.02	0.01
CH <sub>3</sub> CHO	1.67 ± 0.04	0.02
C <sub>2</sub> H <sub>5</sub> OH	2.26 ± 0.05	0.02
C <sub>4</sub> H <sub>10</sub>	2.71 ± 0.03	0.01

$\sigma$  standard deviation

## **CHAPTER III**

# **RESULTS AND DISCUSSION**

## **PART I**

# **THE OZONE SENSITIZED METHANE-OXYGEN REACTION**

### 3.1. Ozone concentration generated by different methods and the reaction results in Reaction System I

#### 3.1.1. The spark method

The concentration of ozone generated by the spark method at 1 atm and room temperature is presented in Table 3.1-1.

Table 3.1-1. Concentration of ozone generated by the spark method at 1 atm and room temperature

flow rate of O <sub>2</sub> (mL/ min at NTP)	O <sub>3</sub> in O <sub>2</sub> (wt) %
5.62	0.038
10.20	0.035
21.57	0.036

Although the sound of the spark was heard clearly and a strong ozone odor could be detected by the nose, the ozone concentration generated by this method, as can be seen from Table 3.1-1, was very low, and it seemed to be independent of the O<sub>2</sub> flow rate in the range of 5.62 mL/min to 21.57 mL/min so that the low concentration of ozone obtained was limited by the method itself, not by O<sub>2</sub> flow rate. This mixture of O<sub>3</sub> and O<sub>2</sub> was mixed with methane and then introduced into the reactor in Reaction System I at the following reaction conditions:

Experiment No. A

O <sub>2</sub> in feed-gas	8 mol %
Total flow rate	118 mL/min (STP)

Reaction temperature 470 °C  
 Reaction pressure 1 atm  
 Residence time 0.09 min.

No methanol was detected in the output gas. There seemed to be three possible reasons for this result: (a) the ozone concentration in oxygen generated by the spark was too low to initiate the partial oxidation of methane to methanol, (b) the reaction temperature was too high so that ozone was almost completely decomposed before entering the reaction zone and (c) the total flow rate was too high (i.e. the residence time in the reactor was too short) so that the conversion of methane was too low and consequently, the concentration of methanol in the output gas was too low to be detected by the analysis instrument (HP G.C.). In the next experiment, the reaction temperature and flow rate were reduced and the ozone was generated by a different method.

### 3.1.2. The silent discharge

The concentration of ozone generated by the silent discharge was much higher than that by the spark method. At room temperature, O<sub>2</sub> flow rate 7.27 mL/min. and 1 atm, 8.47 (wt) % O<sub>3</sub> in O<sub>2</sub> was found after pure O<sub>2</sub> passed through the ozone generator. This means that the concentration of ozone obtained was about 220 times higher than that obtained in the spark apparatus. Unfortunately, although the concentration of ozone generated by this method was high, no methanol in the output gas was detected by the HP G.C. at the following reaction conditions:

Experiment No. B

feed-gas	O <sub>2</sub>	8.082 mol %
	N <sub>2</sub>	2.289 mol %
	CH <sub>4</sub>	89.629 mol %
flow rate		46.48 ml/min (STP)
reaction temperature		355 °C



residence time 0.27 min.

Even when the flow rate was decreased to 6.20 mL/min (residence time 2.04 min.), no methanol (only traces of CO and H<sub>2</sub>O) was observed in the output gas.

In view of these experimental results it was considered that the following causes appeared to account for the absence of methanol.

(a) The residence time in the reactor was still too short so that the conversion of methane in the reactor was very low and the concentration of methanol in the output gas was too low to be detected.

(b) The reactor in this reaction system was made from steel material which is a very good conductor for heat. This made the six-port block just above the reactor and the pre-reaction zone very hot so that ozone was almost completely decomposed in this zone before it could reach the reaction zone.

(c) The reaction temperature was relatively low.

It was clear that a reactor with relatively large reaction volume and made from a material with relatively poor heat conductivity was needed to increase the conversion of methane and reduce the decomposition of ozone outside the reaction zone.

### **3.2. Possibility of ozone initiation tested in Reaction System II**

In this reaction system a Pyrex glass reactor with the reaction volume 120.7 mL was used to test the possibility of ozone initiation.

Seven experiments were carried out. The reaction conditions and methanol (area %) in the output gas obtained are summarized in the Table 3.2-1.

Without ozone in the feed-gas (i.e. the ozone generator was off), no methanol was detected even when the reaction temperature reached 401 °C. However, with ozone in the feed-gas (i. e. the ozone generator was on) significant methanol (0.304 area %) was observed in the output gas at reaction temperature 380 °C. When the reaction results

obtained with ozone in the feed-gas were compared with those obtained without ozone in the feed-gas, it was clear that in all the cases at the reaction conditions used, ozone enhanced the formation of methanol during the reaction. Although the mass balance of the reactions was not carried out due to the low conversion of methane and the analysis performed by sampling with a heated glass syringe and injecting the sample into the G.C. manually, the results were sufficient to draw the conclusion that ozone can initiate the reaction of methane with oxygen.

Table 3.2-1. Comparison of the concentration of  $\text{CH}_3\text{OH}$  (area %) in output gas without  $\text{O}_3$  and with  $\text{O}_3$  in feed-gas ( $\sim 8$  wt %  $\text{O}_3$  in  $\text{O}_2$ )

experiment number	$\text{O}_2$ in feed-gas (area %)	flow rate (mL/min)	residence time (min)	reaction temp. ( $^{\circ}\text{C}$ )	$\text{CH}_3\text{OH}$ in output gas (area %)	
					no $\text{O}_3$ in feed-gas	with $\text{O}_3$ in feed-gas
14	8.963	12.52	3.91	401	Nil	0.278
15	9.839	8.02	6.28	382	Nil	
16	9.839	8.02	6.06	405		0.350
17	9.839	8.02	5.81	434		0.530
18	8.466	9.66	4.83	434	0.202	
19	8.466	9.66	5.23	380		0.304
20	9.396	8.56	5.23	464	0.775	1.025

### 3.3. Ozone sensitized methane partial oxidation in Reaction System III

The ozone concentration in the oxygen generated by the double silent discharge generators when the pure  $O_2$  passed through the generators was measured by the method explained in Chapter II using  $N_2$  to substitute for  $CH_4$  in the feed-gas mixture in order to imitate the actual reaction conditions in the feed-gas mixture during the reaction. The reactor was kept at room temperature, the primary of the high voltage transformer at 115 V (the secondary voltage:  $\sim 15$  kV) and the gas mixture was sampled at the entrance of the reactor and at the exit of the reactor. The results are shown in Table 3.3-1.

Table 3.3-1. Ozone concentration before and after the reactor at room temperature and 1 atm.

experiment number	$O_2$ in gas mixture (mol %)	flow rate of gas mixture (mL/min) at STP	pressure in generator (atm)	$O_3$ in $O_2$ (wt) %	
				before reactor	after reactor
41	7.305	15.98	1.4	8.4	
42	7.305	16.97	1.3	8.7	
43	7.414	11.70	1.3	8.1	
44	7.414	11.05	1.3		7.5
45	7.554	16.82	1.4		7.9
46	7.921	16.43	1.4	8.3	
47	15.884	17.88	1.4	7.9	
48	3.356	16.02	1.4	8.4	

As can be seen in Table 3.3-1, about eight percent (weight) ozone in the O<sub>2</sub> was obtained at the entrance of the reactor. When the gas mixture passed through the reactor, some ozone was lost and its concentration was reduced, but not significantly.

The results obtained in Reactor II and Reactor III at similar reaction conditions are presented in Table 3.3-2.

Table 3.3-2. Comparison of the efficiency of the two Pyrex glass reactors

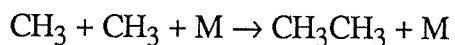
exp. No.	reaction condition					conversion of CH <sub>4</sub> (%)	selectivity of CH <sub>3</sub> OH (%)
	reactor	O <sub>2</sub> in feed (mol %)	RT* (min)	temp (°C)	P* (atm)		
24	II	7.55	7.76	381	1.2	0.536	20.6
32	III	7.43	5.13	375	1.3	0.827	30.3

RT\* = Residence time

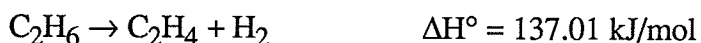
P\* = Reaction Pressure

It is clear that Reactor III was better than Reactor II. Therefore all the experiments, except for experiment 24, were conducted in Reactor III.

The major products detected in the output gas were methanol, formaldehyde, water, carbon monoxide, and carbon dioxide. Formic acid was expected in the products, but was not detected. Perhaps its concentration was too low to be detected by the analysis method. Ethane was always found in the output gas but the concentration was very low and generally increased with increase in the reaction temperature. Ethane was probably formed by the recombination of two methyl radicals.

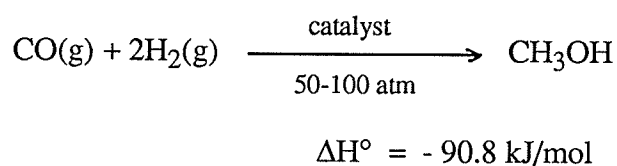


Ethylene was not detected below the reaction temperature of 460 °C. At higher temperatures traces of ethylene were detected and its concentration went up with the increase in the reaction temperature. This indicated that ethylene was formed by dehydrogenating ethane.



Since the dehydrogenation was an endothermic reaction, it needed a high temperature to provide enough energy to make the reaction proceed, thus the yield of ethylene increased with the reaction temperature.

The selectivity of methanol was usually less than 50%. A considerable amount of carbon monoxide was found in the products. Carbon monoxide is a useful chemical and can be converted to the methanol by the following process,



and the energy released in the process can be recovered and utilized. If the selectivity included methanol, formaldehyde, and carbon monoxide, this selectivity was higher than 85 % (usually higher than 90 %) as shown in Figure 3.3-3.

### 3.3.1. Effects of reaction temperature

This set of the experiments (#32 - #36) were carried out at the following reaction conditions:

Residence time: 5.13 ~ 5.78 min.

Reaction pressure: 1.3 atm.

Ozone concentration in oxygen: ca. 8 (wt) %

Oxygen concentration in the feed-gas: 7.36 ~ 7.48 (mol)%,

and the results are given in Appendix B.

### Conversion

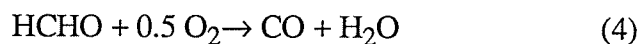
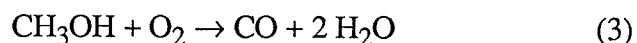
The conversion of both methane and oxygen was found to increase with the increase of the reaction temperature (Figure 3.3-1). At reaction temperatures lower than 430 °C, the increase of the conversions of both methane and oxygen with reaction temperature was slow. The conversion of methane increased from 0.827 % (375 °C) to 1.78 % (430 °C) and the conversion of oxygen from 12.1 % (375 °C) to 21.9 % (430 °C). However, at reaction temperatures higher than 430 °C the conversion of both methane and oxygen increased rapidly and almost linearly with the reaction temperature, especially conversion of oxygen. From 430 °C to 490 °C the conversion of oxygen increased from 21.9 % (430 °C) to 85.9 % (490 °C) and the conversion of methane increased from 1.78% (430 °C) to 7.34% (490 °C).

### Selectivity

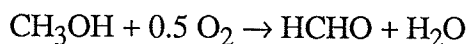
The change in methanol selectivity (based on carbon) with the reaction temperature had the same pattern with that based on oxygen (Figure 3.3-2). At reaction temperatures lower than 387 °C the selectivity of methanol increased with reaction temperature. At the reaction temperatures higher than 387 °C, however, it decreased with increase in the reaction temperature. There was a maximum value of the selectivity of methanol (31.0 %) at 387 °C. This implies that methanol is an intermediate product in the oxidation sequence from methane to carbon dioxide. In the lower reaction temperature range (below 387 °C) increase in the reaction temperature will raise the reaction rates of both the desired reaction



and the undesired reactions, for example,



but the rate of Reaction (1) was increased more quickly than the sum of the rates of the undesired reactions so that the selectivity of methanol increased with the rise of reaction temperature. In the higher reaction temperature range (above 387 °C) the sum of the rates of the undesired reactions increased more quickly than that of Reaction (1), particularly the rate of the formation of carbon monoxide. As shown in Figure 3.3-3, rapid increase in the selectivity of carbon monoxide with the increase of reaction temperature caused the decrease of the selectivity of methanol. It seemed that too high a reaction temperature favored the formation of carbon monoxide. Since the selectivity of formaldehyde was generally parallel to the selectivity of methanol (Figure 3.3-3), formaldehyde was probably produced by the further oxidation of methanol, i. e.,



The selectivity of carbon dioxide was very low and, generally, increased very slowly with reaction temperature, as shown in Figure 3.3-3.

### Yield

The variation of the yield of methanol with reaction temperature is shown in Figure 3.3-4. Although the conversion of methane was found always to increase with reaction temperature in the the range from 375 °C to 490 °C, the selectivity of methanol decreased with the increase of reaction temperature at the higher temperature range. This resulted in a maximum yield of methanol which was observed at about 458 °C (Figure 3.3-4). The temperature at the maximum yield (458 °C) was higher than the temperature at the maximum selectivity (387 °C).

### 3.3.2. Effects of residence time

In order to investigate the effect of residence time on the results of the reaction, the flow rate of the feed-gas mixture was raised to about 140% of that used in the last set of the experiments (#32 - #36), namely, the residence time was reduced to about 40% that of the last set. This set of experiments (#37 -#40) were run in the following conditions:

Residence time: 3.36 ~ 3.76 min.

Reaction pressure: 1.35 ~ 1.40 atm.

Ozone concentration in oxygen: ca. 8 (wt)%

Oxygen concentration in feed-gas: 6.68 ~ 7.73 (mol)%

The results were plotted against the reaction temperature. The pattern obtained was similar to that of the last set of experiments. The conversion of methane and oxygen increased with reaction temperature (Figure 3.3-5). There seemed to be a maximum value in the selectivity of methanol which is probably at below 400 °C (Figure 3.3-6). A maximum value in the methanol yield (based on carbon) was observed at about 442 °C (Figure 3.3-7).

An important discovery was that the selectivity of methanol increased as the residence time was decreased. In Figure 3.3-9 the lines with solid circles and squares represent the selectivity of methanol obtained at the residence time 3.36~3.76 min. and the lines with empty circles and squares represent the selectivity of methanol obtained at the residence time 5.13~5.78 min. At almost all the reaction temperatures the selectivity of methanol at shorter residence time was higher than that at longer residence time, especially in the lower temperature range. When the residence time was decreased from 5.35 min to 3.76 min at the reaction temperature of 401 °C, the selectivity of methanol increased from 29.3 % to 43.6 % (based on carbon). This indicated that the preservation of methanol was favored by shorter residence time. This reduced the possibility of further oxidation of methanol to carbon monoxide and most probably contributed to this increase in the methanol selectivity. The higher selectivity of methanol would have been obtained if the



residence time could have been reduced further. Unfortunately, the further decrease in residence time (i. e. further increase flow rate) was limited by the back-pressure caused by the sampling valve of the gas chromatograph.

According to the general rules of chemical kinetics the conversions of the reactants usually should decrease as the residence time in the reactor is decreased when the reaction temperature and other reaction conditions are kept the same. However, very strange results were obtained in this research. The conversions of oxygen at shorter residence times were higher than at longer residence times (Figure 3.3-8). We found a reasonable explanation for this strange phenomenon after the characteristics of this particular reaction and the reaction system used were carefully examined.

Although the concentration of ozone was kept almost constant in the feed-gas in the mixing tube as the residence time was changed, the concentration of ozone that reached the reaction zone would be different due to decomposition in the line between the mixing tube and the reaction zone. It is well known that the ozone is easily decomposed at high temperature. There was a temperature transition section (from the entrance of the furnace for the reactor to the reaction zone) in which the temperature changed from room temperature to near reaction temperature. The more quickly ozone passed this temperature transition section, the less decomposed. The initiation effect of ozone depends on the concentration of ozone which reaches the reaction zone but not on that in the feed-gas outside of the reactor. When the residence time in the reactor was reduced (the flow rate of the feed-gas was increased), ozone could more quickly pass through the temperature transition section so that less decomposition of ozone occurred and more ozone reached the reaction zone to initiate the reaction. Consequently, the conversion became greater as the residence time decreased.

### 3.3.3. Effect of oxygen concentration in feed-gas

The effect of oxygen concentration in feed-gas was studied at the reaction temperature 402 °C, reaction pressure 1.45 ~ 1.50 atm., ozone concentration in oxygen ca. 8 (wt) %, and residence time 3.81 ~ 4.24 min. The conversion of oxygen fell with the increase of oxygen concentration in the feed-gas. However, the conversion of methane, generally, increased with oxygen concentration (Figure 3.3-10).

The selectivity of methanol was found to decrease with the increase of oxygen concentration (Figure 3.3-11).

The methanol yield (based on oxygen) dropped rapidly with increase in oxygen concentration in the feed-gas (Figure 3.3-12) since both the conversion and selectivity decreased with oxygen concentration. But the yield of methanol (based on carbon) was not greatly influenced and appeared independent of oxygen concentration in the feed-gas because, although the selectivity (based on carbon) diminished with oxygen concentration, the conversion of methane went up with oxygen concentration in the feed-gas.

### 3.3.4. The variation of the selectivity of methanol with the conversion of methane

The change of the selectivity of methanol (based on carbon) with the conversion of methane is given in Table 3.3-4. A plot of the  $\text{CH}_3\text{OH}$  selectivity (based on carbon) vs the  $\text{CH}_4$  conversion is given in Figure 3.3-13.

It was found that the selectivity of methanol generally increased with the decrease of the conversion of methane. In the range of the methane conversion higher than 3% the methanol selectivity increased slowly as the methane conversion decreased, but in the range of the methane conversion lower than 1 % the methanol selectivity increased rapidly with decrease of the methane conversion.

### 3.3.5. Effect of ozone concentration

It was reported<sup>42</sup> that the concentration of ozone generated decreased with increase in pressure, and it was found that in our laboratory, no ozone was detected at high pressure using the spark ozone generation method. However, the reaction pressure favors the formation of methanol in the homogeneous reaction of methane with oxygen. Is it possible for ozone to initiate the reaction of methane with oxygen at pressures slightly higher than atmosphere at which the concentration of ozone generated will be lower? In order to determine the minimum ozone concentration at which the initiation effects can be detected, the influence of ozone concentration on the conversion of methane was investigated by reducing the voltage charged on the generator.

It was found that the conversion of methane increased with increase in the voltage charged in the generator, namely, with increase in ozone concentration (Table 3.3-3) at the reaction temperature of 380 °C, residence time in the reactor of ~4 min., and O<sub>2</sub> concentration in the feed-gas of ~6 %.

Table 3.3-3. Effect of ozone concentration on the methane conversion

Exp. No.	Pressure in the generator (atm)	Voltage on the primary of the high voltage transformer (V)	O <sub>3</sub> (wt %)	CH <sub>4</sub> conversion (%)
78	1.8	61.7		no rxn
79	1.8	71.0		very little
85	1.8	71.5	0.0026	
80	1.8	86.5		0.773
84	1.8	85.6	1.5	

With ~1.5% O<sub>3</sub> in O<sub>2</sub> considerable conversion of methane was observed compared to no reaction being detected without O<sub>3</sub> in O<sub>2</sub>. Therefore, there is a possibility that the reaction of methane with oxygen can be initiated by O<sub>3</sub> at about 2 atmosphere pressure if the concentration of ozone generated can reach ~1.5%.

### 3.3.6. Mass balance

#### (a) Expressions for calculation of conversion, selectivity and yield

The conversions of methane and oxygen, selectivities of methanol and other products, and yields of products were calculated by using the following overall expressions:

$$\text{CH}_4 \text{ conversion (mol \%)} = \frac{\sum \text{C products}}{\text{CH}_{4_{\text{out}}} + \sum \text{C products}} \times 100$$

where  $\sum \text{C products} = \text{CO} + \text{CO}_2 + \text{HCHO} + \text{CH}_3\text{OH} + 2 \times \text{C}_2\text{H}_4 + 2 \times \text{C}_2\text{H}_6$

and CO, CO<sub>2</sub>, HCHO, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>4<sub>out</sub></sub> refer to the mole percentages of these compounds in the exit stream from the reactor.

$$\text{O}_2 \text{ conversion (mol \%)} = \frac{\sum \text{O products}}{2 \times \text{O}_{2_{\text{out}}} + \sum \text{O products}} \times 100$$

where  $\sum \text{O products} = \text{CO} + 2 \times \text{CO}_2 + \text{HCHO} + \text{CH}_3\text{OH} + \text{H}_2\text{O}$

and CO, CO<sub>2</sub>, HCHO, H<sub>2</sub>O, CH<sub>3</sub>OH and O<sub>2<sub>out</sub></sub> refer to the mole percentages of these compounds in the exit stream from the reactor.

$$\text{CH}_3\text{OH selectivity (based on carbon, mol \%)} = \frac{\text{CH}_3\text{OH}}{\sum \text{C products}} \times 100$$

$$\text{CH}_3\text{OH selectivity (based on oxygen, mol \%)} = \frac{\text{CH}_3\text{OH}}{\sum \text{O products}} \times 100$$

On a similar basis, the selectivities of the other products were calculated.

$\text{CH}_3\text{OH}$  yield (based on carbon, mol %) =

$$\frac{\text{CH}_3\text{OH selectivity (based on carbon, mol \%)} \times \text{CH}_4 \text{ conversion (mol \%)}}{100},$$

$\text{CH}_3\text{OH}$  yield (based on oxygen, mol %) =

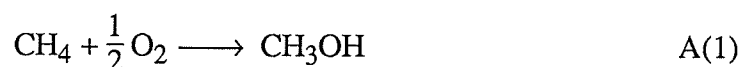
$$\frac{\text{CH}_3\text{OH selectivity (based on oxygen, mol \%)} \times \text{O}_2 \text{ conversion (mol \%)}}{100}$$

The yields of the other products were calculated on a similar basis.

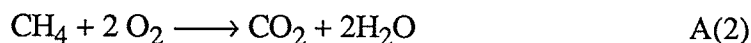
The calculated results of the conversions, selectivities and yields for each experiment are given in Appendix B.

It was found that the selectivity of methanol based on carbon always was higher than that based on oxygen. This can be explained as follows:

If only the reaction



proceeds in the reaction system, the selectivity of methanol based on carbon will be equal to that based on oxygen. However, in addition to the desired Reaction A(1) there are undesired reactions proceeding in the reaction system. For example, the reaction



Supposing the reaction rate of Reaction A(1) equals that of Reaction A(2), i.e.,

$$-(dC_{\text{CH}_4} / dt)_1 = -(dC_{\text{CH}_4} / dt)_2$$

then  $\text{CH}_3\text{OH}$  selectivity (based on carbon, mol %) =  $\frac{1}{2} \times 100 = 50 \%$ ,

but  $\text{CH}_3\text{OH}$  selectivity (based on oxygen, mol %) =  $\frac{1}{5} \times 100 = 20 \%$

Therefore, due to the undesired reactions which usually occurred in the reaction system, the selectivity of methanol based on oxygen was lower than that based on carbon.

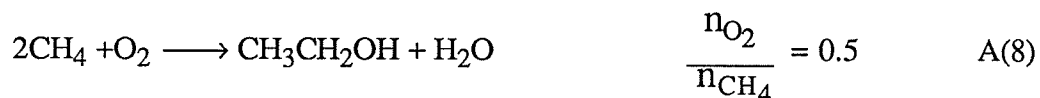
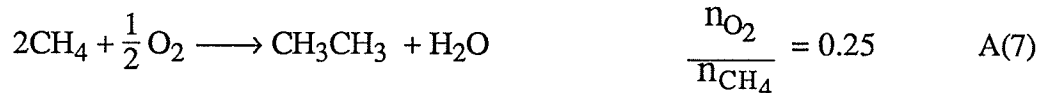
Another general rule observed was that the conversion of oxygen was higher than that of methane.

If the following reactions occurred in the reaction system,



the ratio of  $n_{\text{O}_2}$  to  $n_{\text{CH}_4}$  would be equal to or more than one. On the other hand, if the reaction of methane with oxygen occurred through





the ratio of  $n_{\text{O}_2}$  to  $n_{\text{CH}_4}$  would be less than one.

Because the experimental data indicated that the majority of methane (more than 80 %) was consumed by reactions A(1), A(3) and A(5), the ratio of  $n_{\text{O}_2}$  to  $n_{\text{CH}_4}$  usually was between 0.5 and 1.5.

The conclusion can be drawn that  $\frac{n_{\text{O}_2}}{n_{\text{CH}_4}}$  cannot exceed two because the maximum value of  $\frac{n_{\text{O}_2}}{n_{\text{CH}_4}}$  is two according to the above inference.

Since the conversion was defined as

$$\text{conversion (mol \%)} = \frac{n_{\text{consumed}}}{n_{\text{in}}} \times 100$$

the magnitude of the conversion depends not only on moles consumed during the reaction but also on the moles entering the reactor. Although the ratio of  $n_{\text{O}_2}$  consumed to  $n_{\text{CH}_4}$  consumed in the reactor would be less than one (for instance, 0.25 - 1), the concentration of methane in the feed-gas was about ten times higher than that of oxygen in the feed-gas. This made the conversion of oxygen always higher than that of methane.

#### (b) Expression for the calculation of residence time

The residence time in the reactor was calculated by the expression

$$\text{Residence time} = \frac{V_{\text{reactor}} P_{\text{rxn}} T_{\text{room}}}{F_{\text{in}} P_{\text{atm}} T_{\text{rxn}}}$$

where  $F_{\text{in}}$  represents the flow rate of the feed-gas at room temperature and atmospheric pressure, and the subscript rxn refers to reaction.

(c) Equations for the calculation of the material balances of carbon, oxygen and hydrogen

Based on the assumption that the mass of nitrogen which entered the reactor was equal to that of nitrogen leaving the reactor (i.e.,  $N_2$  was used as an internal standard), material balances for carbon, oxygen and hydrogen were arrived at as follows:

$$\text{Since } Y_{N_2, \text{ in}} n_{\text{total, in}} = Y_{N_2, \text{ out}} n_{\text{total, out}}$$

$$n_{\text{total, out}} = Y_{N_2, \text{ in}} n_{\text{total, in}} / Y_{N_2, \text{ out}}$$

where  $n$  refers to the number of moles and  $y$  means mole fraction.

$Y_{N_2}$  was obtained from the results of analysis and  $n_{\text{total, in}}$  was calculated from the equation

$$n_{\text{total, in}} = \frac{F_{\text{in}} P_{\text{atm}}}{RT_{\text{room}}}$$

where  $F_{\text{in}}$  refers to the total flow rate of the feed-gas at room temperature and atmospheric pressure.

Then, the moles of the reactants and products in a unit of time were calculated by the two equations

$$n_{i, \text{ in}} = Y_{i, \text{ in}} n_{\text{total, in}}$$

$$\text{and } n_{i, \text{ out}} = Y_{i, \text{ out}} n_{\text{total, out}}$$

Then, the mass balances were calculated by

$$\frac{M_{C_{\text{out}}}}{M_{C_{\text{in}}}} = \frac{n_{C_{\text{out}}}}{n_{C_{\text{in}}}} = \frac{n_{CH_4_{\text{out}}} + \sum C \text{ products}}{n_{CH_4_{\text{in}}}}$$



where M means mass and

$$\sum C \text{ products} = n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{HCHO}} + n_{\text{CH}_3\text{OH}} + 2 \times n_{\text{C}_2\text{H}_4} + 2 \times n_{\text{C}_2\text{H}_6}$$

$$\frac{M_{\text{O}_{\text{out}}}}{M_{\text{O}_{\text{in}}}} = \frac{n_{\text{O}_{\text{out}}}}{n_{\text{O}_{\text{in}}}} = \frac{2 \times n_{\text{O}_{2\text{out}}} + \sum \text{O products}}{2 \times n_{\text{O}_{2\text{in}}}}$$

$$\text{where } \sum \text{O products} = n_{\text{CO}} + 2 \times n_{\text{CO}_2} + n_{\text{HCHO}} + n_{\text{CH}_3\text{OH}} + n_{\text{H}_2\text{O}}$$

$$\frac{M_{\text{H}_{\text{out}}}}{M_{\text{H}_{\text{in}}}} = \frac{n_{\text{H}_{\text{out}}}}{n_{\text{H}_{\text{in}}}} = \frac{4 \times n_{\text{CH}_{4\text{out}}} + \sum \text{H products}}{4 \times n_{\text{CH}_{4\text{in}}}}$$

$$\text{where } \sum \text{H products} = 2 \times n_{\text{H}_2\text{O}} + 2 \times n_{\text{HCHO}} + 4 \times n_{\text{CH}_3\text{OH}} + 4 \times n_{\text{C}_2\text{H}_4} + 6 \times n_{\text{C}_2\text{H}_6}$$

The calculation of the material balances, based on nitrogen balance, was performed for each experiments (Appendix B). Both an average of the ratio of Mass(out) to Mass (in) and a standard deviation were obtained for carbon, oxygen and hydrogen, and the results are provided below.

$$\frac{M_{\text{C}_{\text{out}}}}{M_{\text{C}_{\text{in}}}} = 0.985 \pm 0.038$$

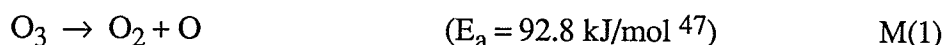
$$\frac{M_{\text{O}_{\text{out}}}}{M_{\text{O}_{\text{in}}}} = 1.027 \pm 0.073$$

$$\frac{M_{\text{H}_{\text{out}}}}{M_{\text{H}_{\text{in}}}} = 0.970 \pm 0.059$$

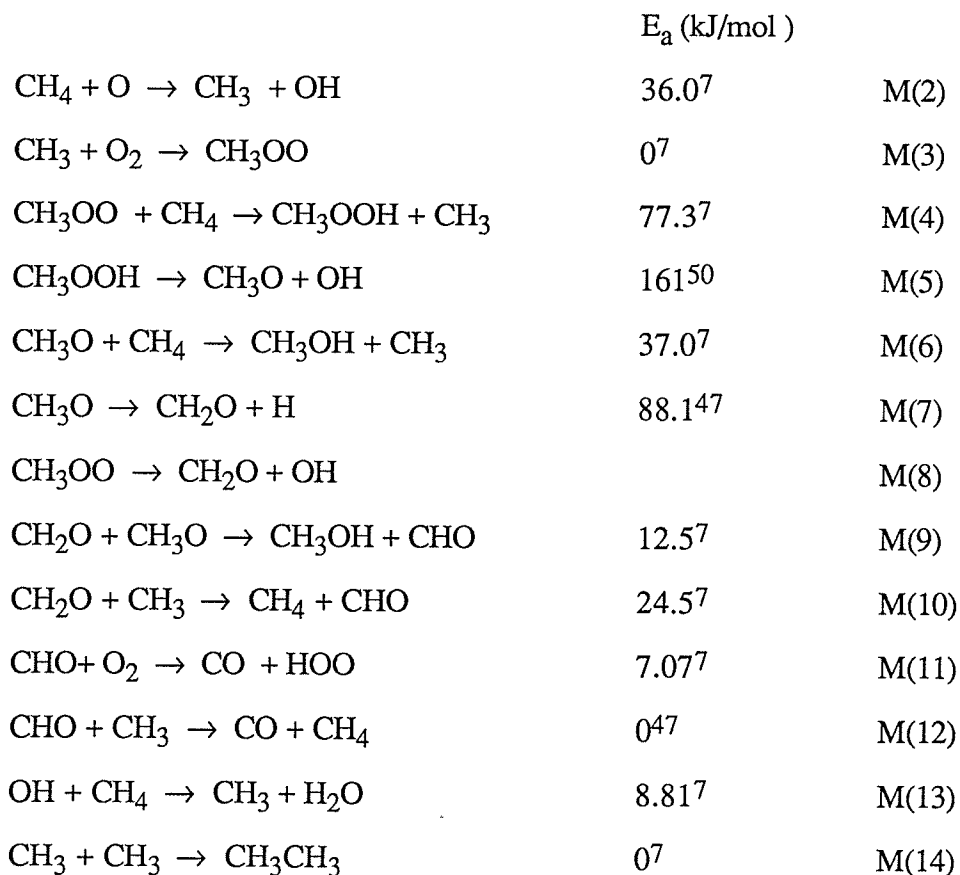
### 3.3.7. Reaction mechanism

(a) At lower reaction temperatures

Based on the observation that no reaction between methane and oxygen was detected at lower reaction temperatures without ozone in the feed-gas but considerable reaction was detected at the same temperature with ozone in the feed-gas, it is clear that the reaction between methane and oxygen was initiated by ozone. The first step was that ozone decomposed to dioxygen and an ground state ( $^3P$ ) oxygen atom



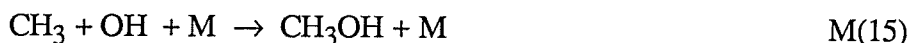
Then, the oxygen atom initiated the reaction between methane and oxygen and the reaction proceeded by a free radical chain reaction mechanism. We believe that the following reactions are included in the reaction mechanism.



etc.

Methanol was produced by Reactions M(6) and M(9). Reaction M(14) accounted for the formation of ethane.

The reaction



was proposed to occur at high pressure<sup>36</sup>. We believe that it may also occur at atmospheric pressure and contributed to some of the formation of methanol.

(b) At higher reaction temperatures

Whether ozone existed in the feed-gas or not, the reaction between methane and oxygen was detected at higher reaction temperatures, but ozone accelerated the reaction and enhanced the formation of methanol. It is therefore reasonable to assume that the reaction of methane with oxygen proceeded via both ozone-initiating reaction and ordinary homogeneous reaction at the higher temperatures.

In addition to Reactions from M(1) to M(15), the following reactions probably occurred at higher temperature:

	$E_a$ (kJ/mol )	
$\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HOO}$	238. <sup>7</sup>	M(16)
$\text{CH}_3\text{-CH}_2 \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}$	178 <sup>53</sup>	M(17)
$\text{CH}_3\text{-CH}_3 + \text{H} \rightarrow \text{CH}_3\text{-CH}_2 + \text{H}_2$	25.9 <sup>53</sup>	M(18)
$\text{CH}_3\text{-CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{-CH}_2 + \text{HOO}$	213 <sup>7</sup>	M(19)
$\text{CH}_3\text{-CH}_2 + \text{O}_2 \rightarrow \text{CH}_2=\text{CH}_2 + \text{HOO}$	16.2 <sup>7</sup>	M(20)

Reaction M(16) is considered as the initial step for the ordinary homogeneous reaction and Reactions from M(17) to M(20) account for the traces of ethylene observed at higher temperatures. The reaction temperatures were in the range where dehydrogenation could occur and the selectivity of ethylene was found to increase with increase in the reaction temperature.

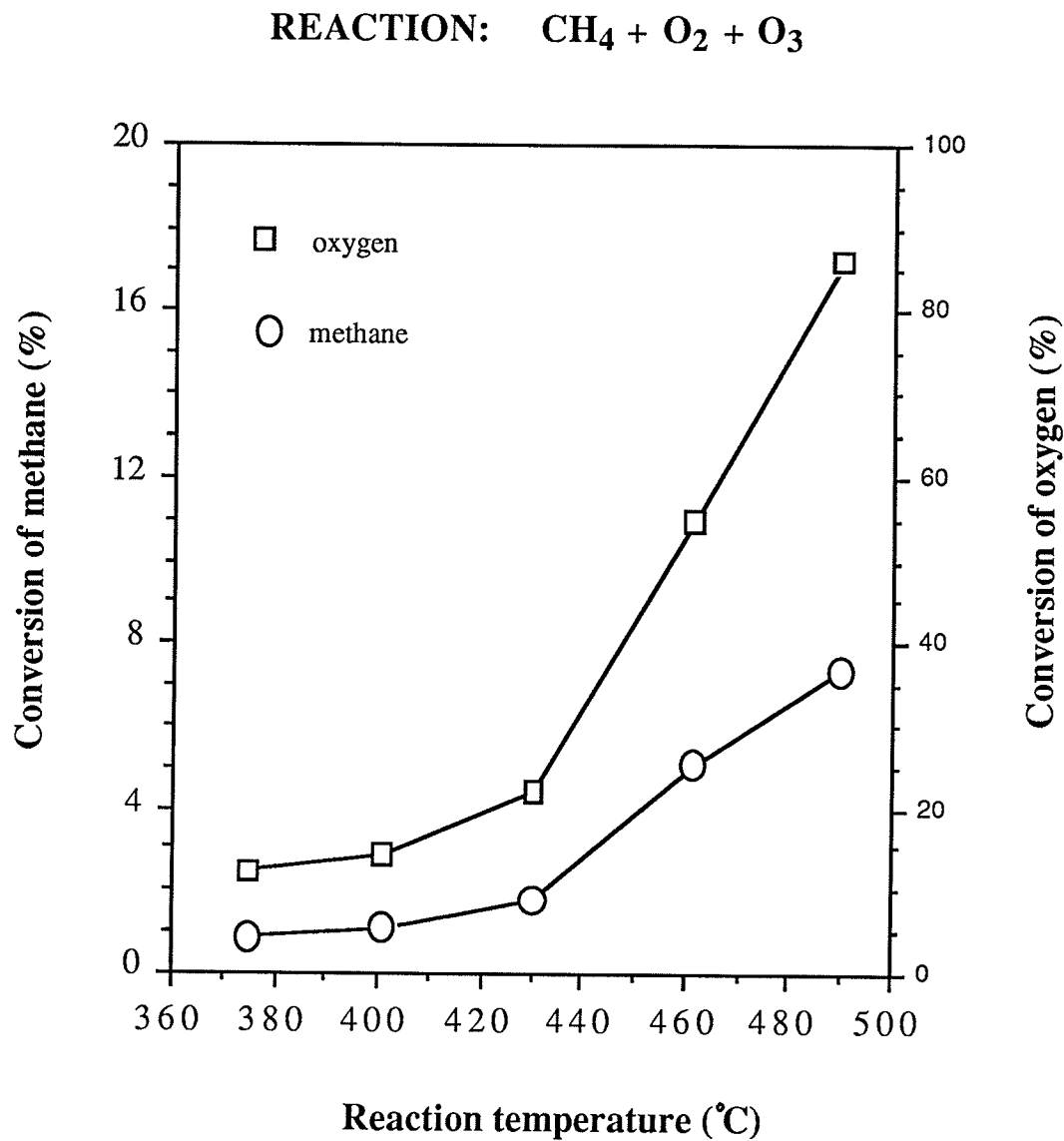


Figure 3.3-1. Variation of the conversion of reactants with reaction temperature

Residence time: 5.13 ~ 5.78 min.    Reaction pressure: 1.3 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in the feed-gas: 7.36 ~ 7.48 mol %

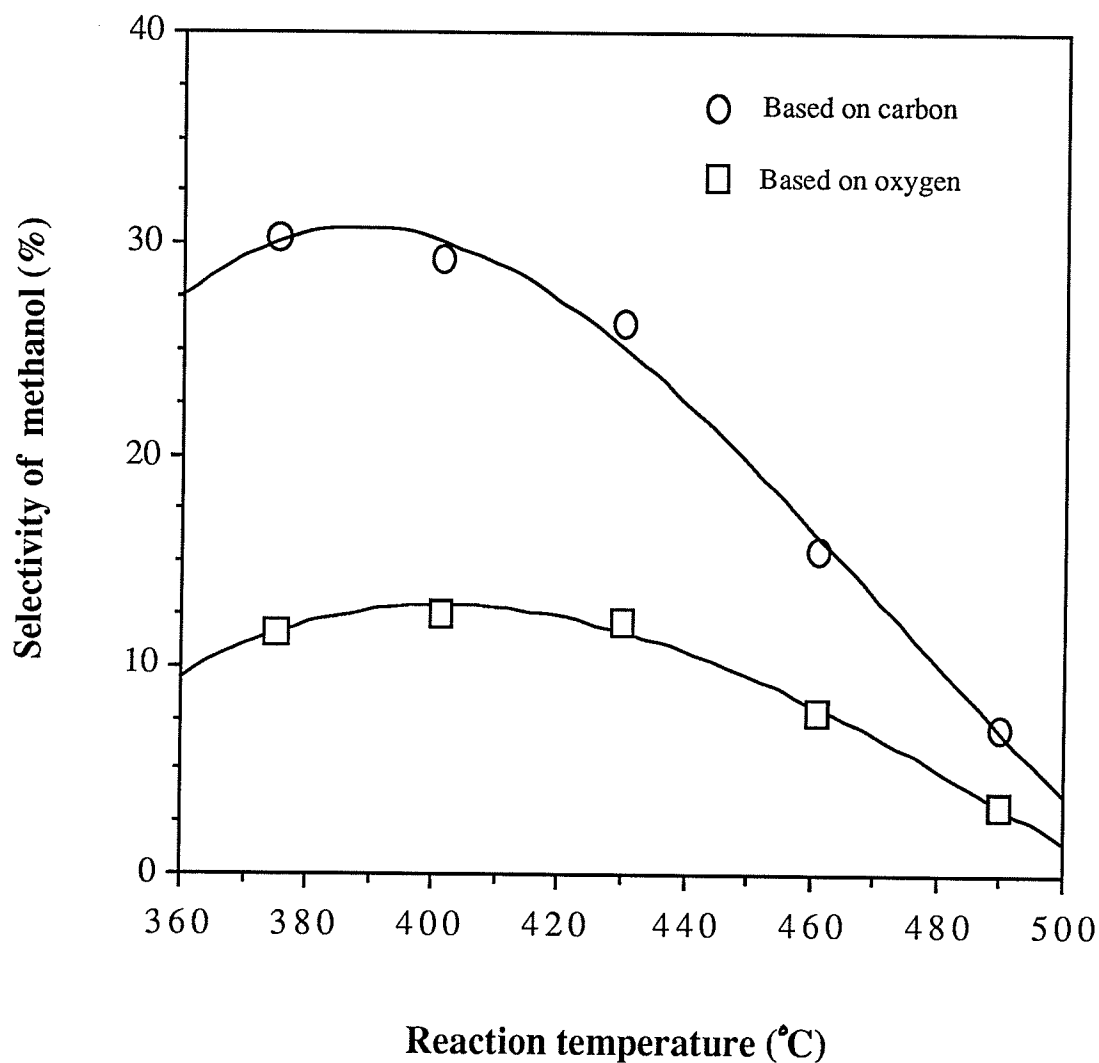


Figure 3.3-2. Variation of methanol selectivity with reaction temperature

Residence time: 5.13 ~ 5.78 min. Reaction pressure: 1.3 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in the feed-gas: 7.36 ~ 7.48 mol %

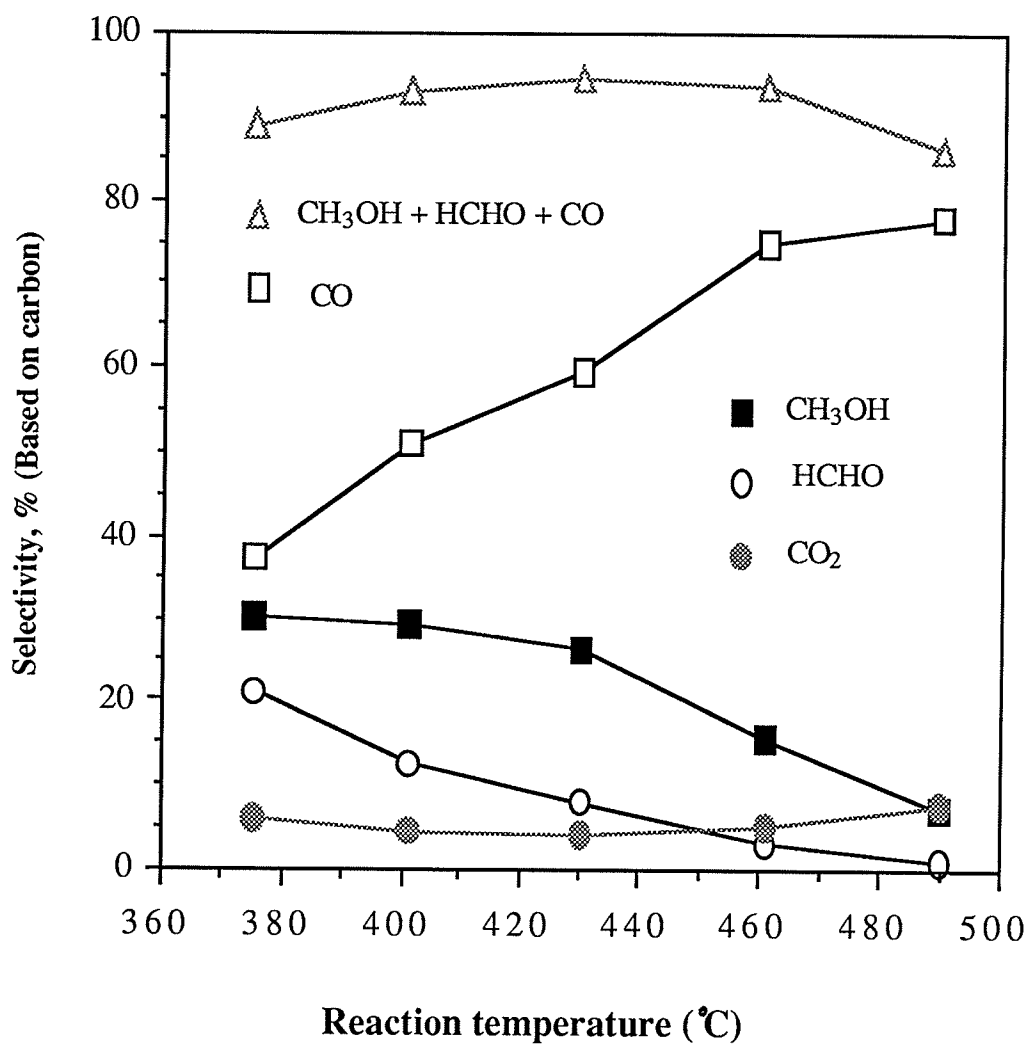


Figure 3.3-3. Variation of selectivity with reaction temperature

Residence time: 5.13 ~ 5.78 min. Reaction pressure: 1.3 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in the feed-gas: 7.36 ~ 7.48 mol %

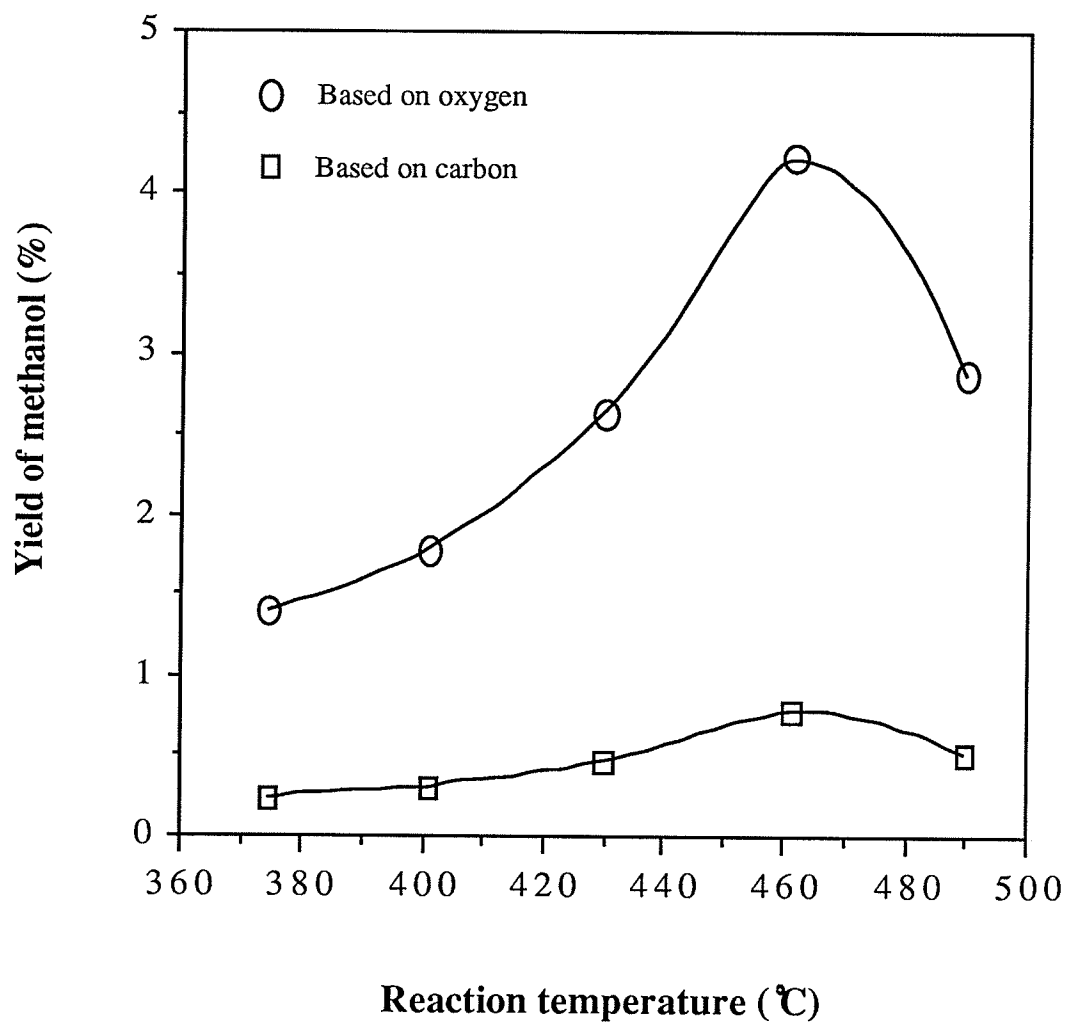


Figure 3.3-4. Variation of methanol yield with reaction temperature

Residence time: 5.13 ~ 5.78 min. Reaction pressure: 1.3 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in the feed-gas: 7.36 ~ 7.48 mol %

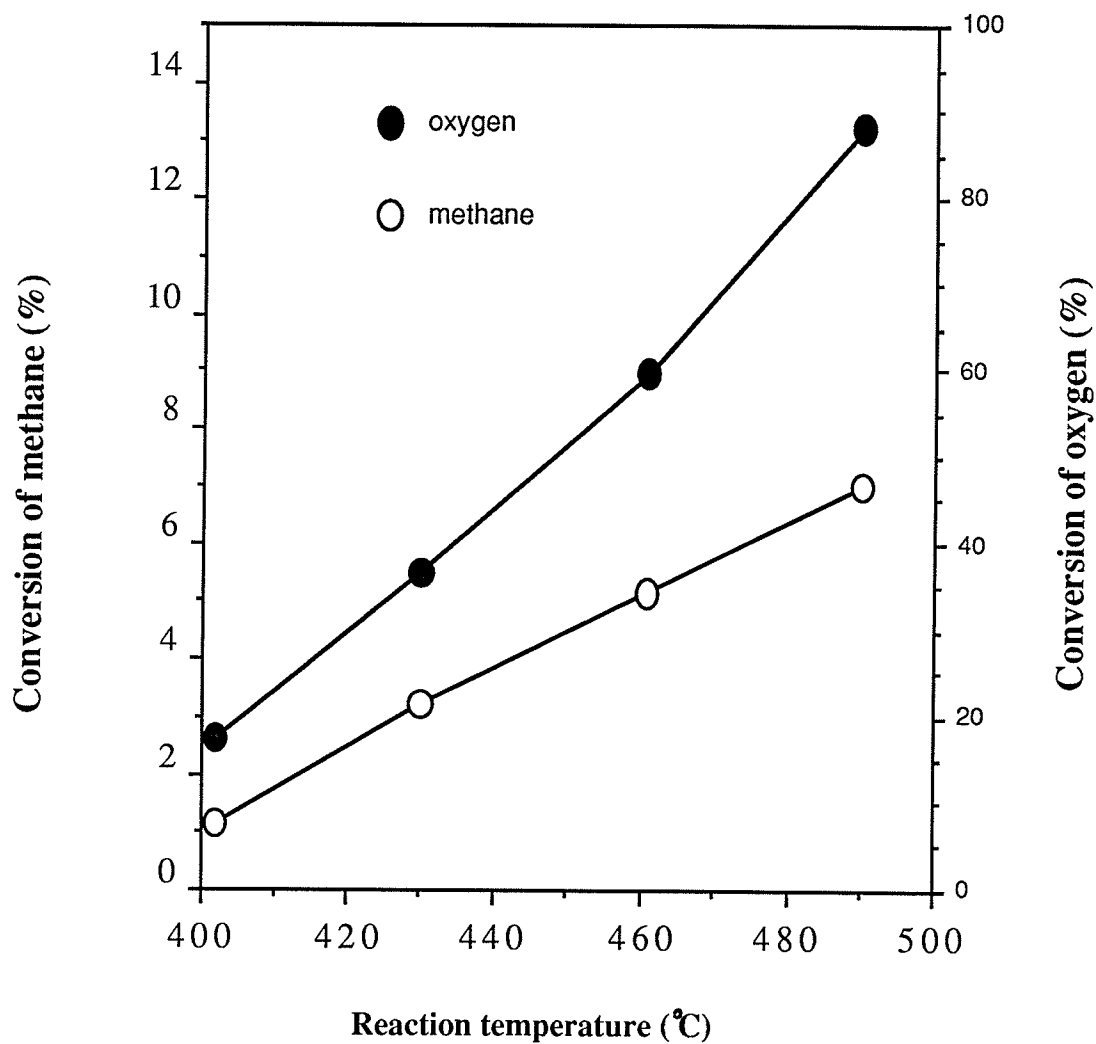


Figure 3.3-5. Variation of the conversion of the reactants with reaction temperature at shorter residence time

Residence time: 3.36 ~ 3.76 min. Reaction pressure: 1.35 ~ 1.40 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in feed-gas: 6.68 ~ 7.73 mol%



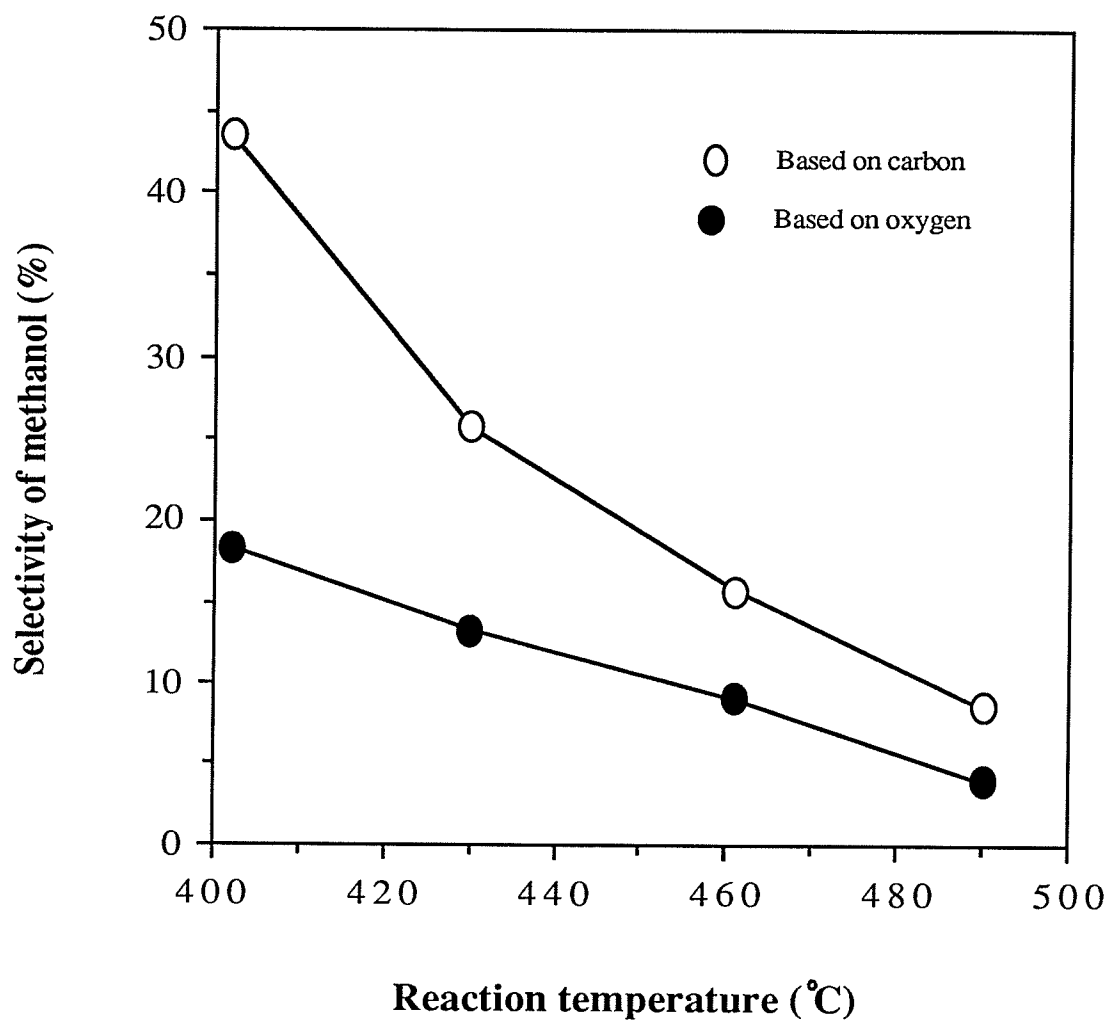


Figure 3.3-6. Variation of methanol selectivity with reaction temperature at shorter residence time

Residence time: 3.36 ~ 3.76 min. Reaction pressure: 1.35 ~ 1.40 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in feed-gas: 6.68 ~ 7.73 mol %

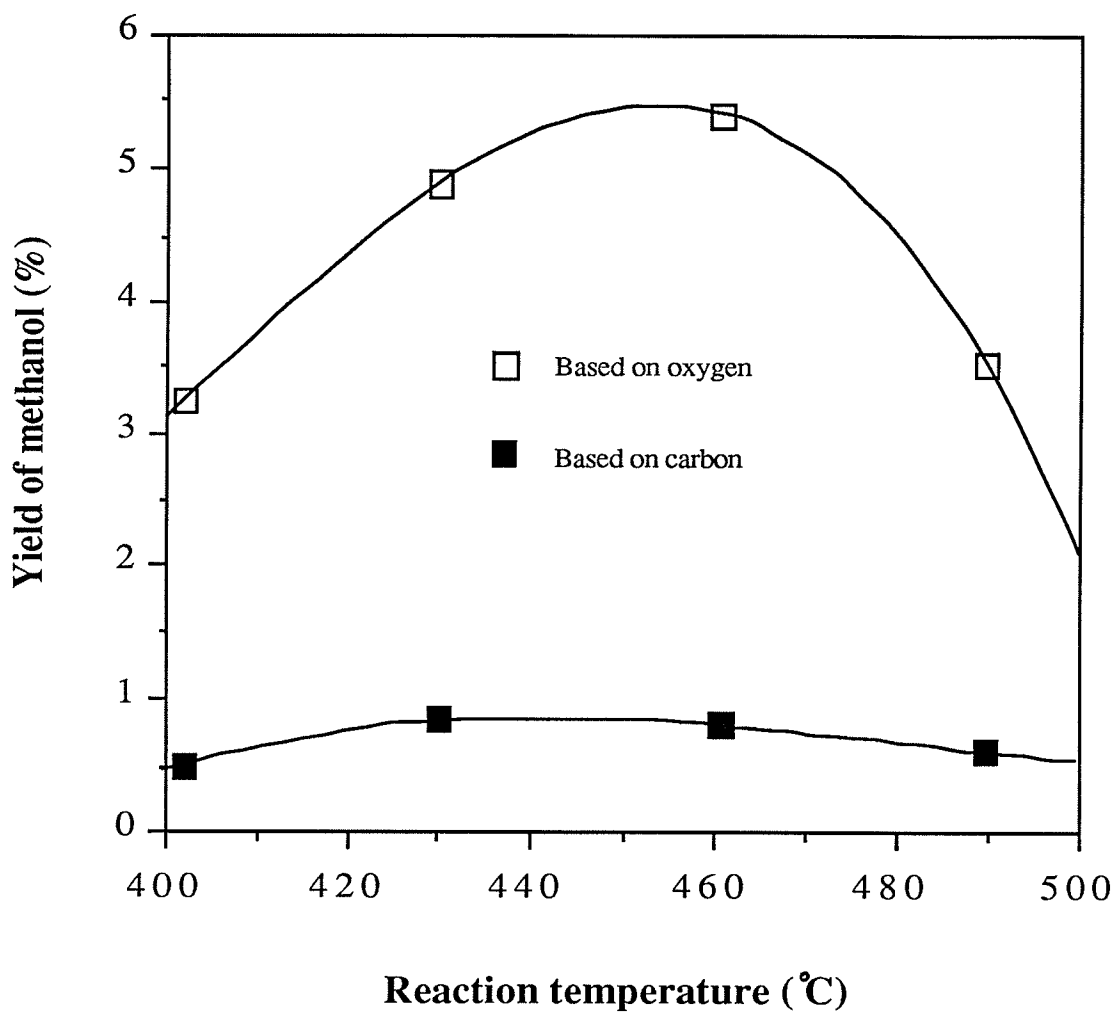


Figure 3.3-7. Variation of methanol yield with reaction temperature at shorter residence time

Residence time: 3.36 ~ 3.76 min. Reaction pressure: 1.35 ~ 1.40 atm.

Ozone concentration in oxygen: ca. 8 wt %

Oxygen concentration in feed-gas: 6.68 ~ 7.73 mol%

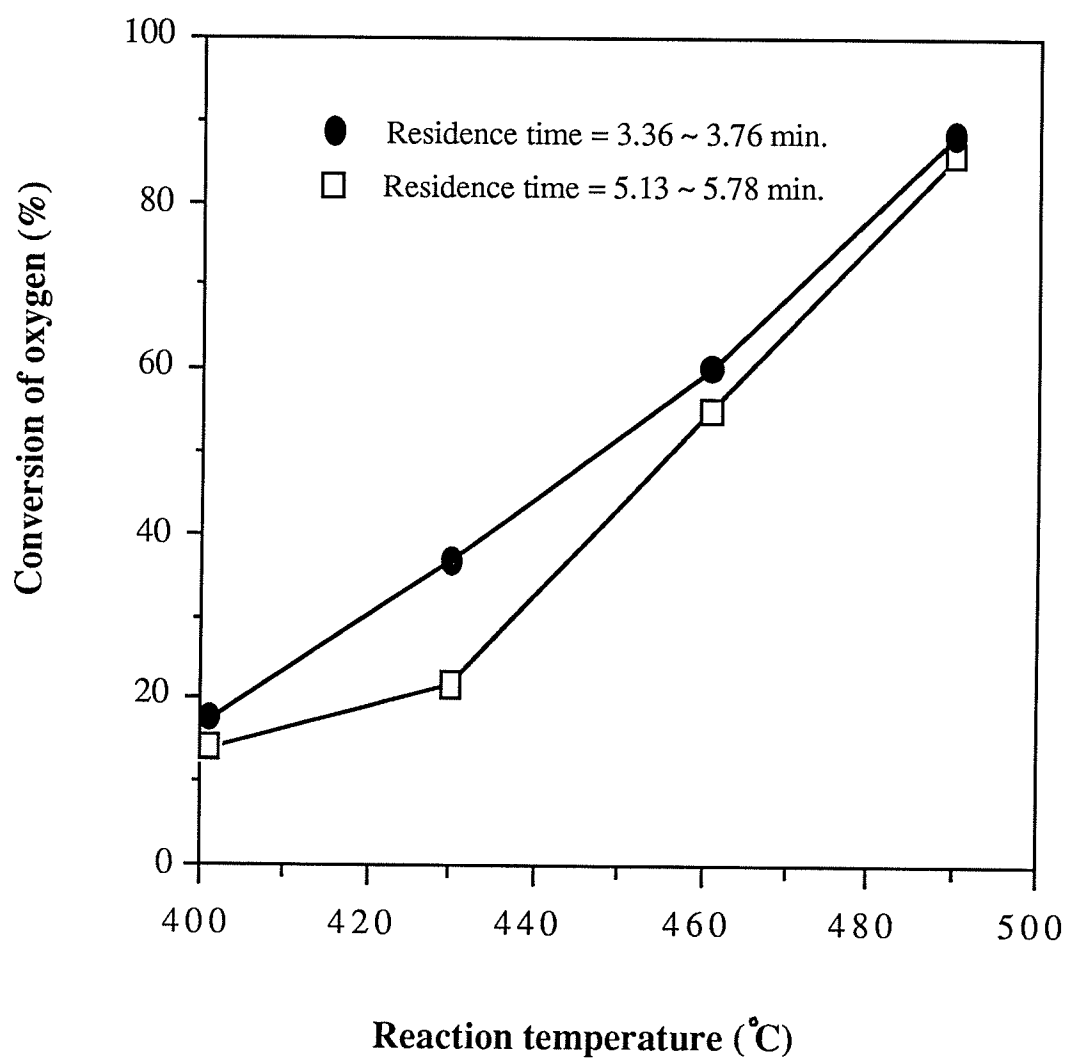
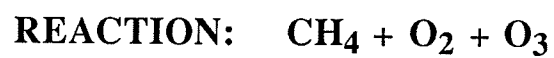


Figure 3.3-8. Variation of oxygen conversion with reaction temperature at different residence time

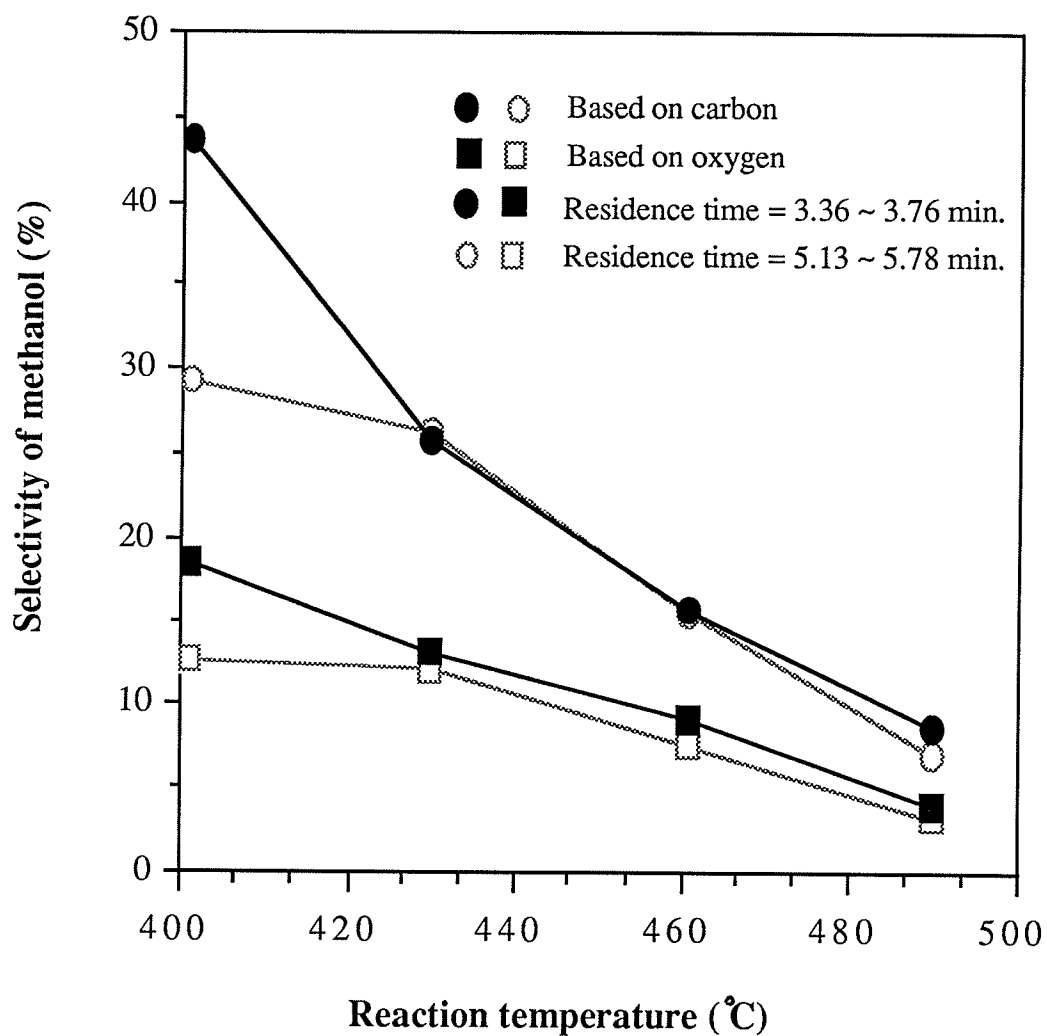


Figure 3.3-9. Variation of  $\text{CH}_3\text{OH}$  selectivity with reaction temperature at different residence time

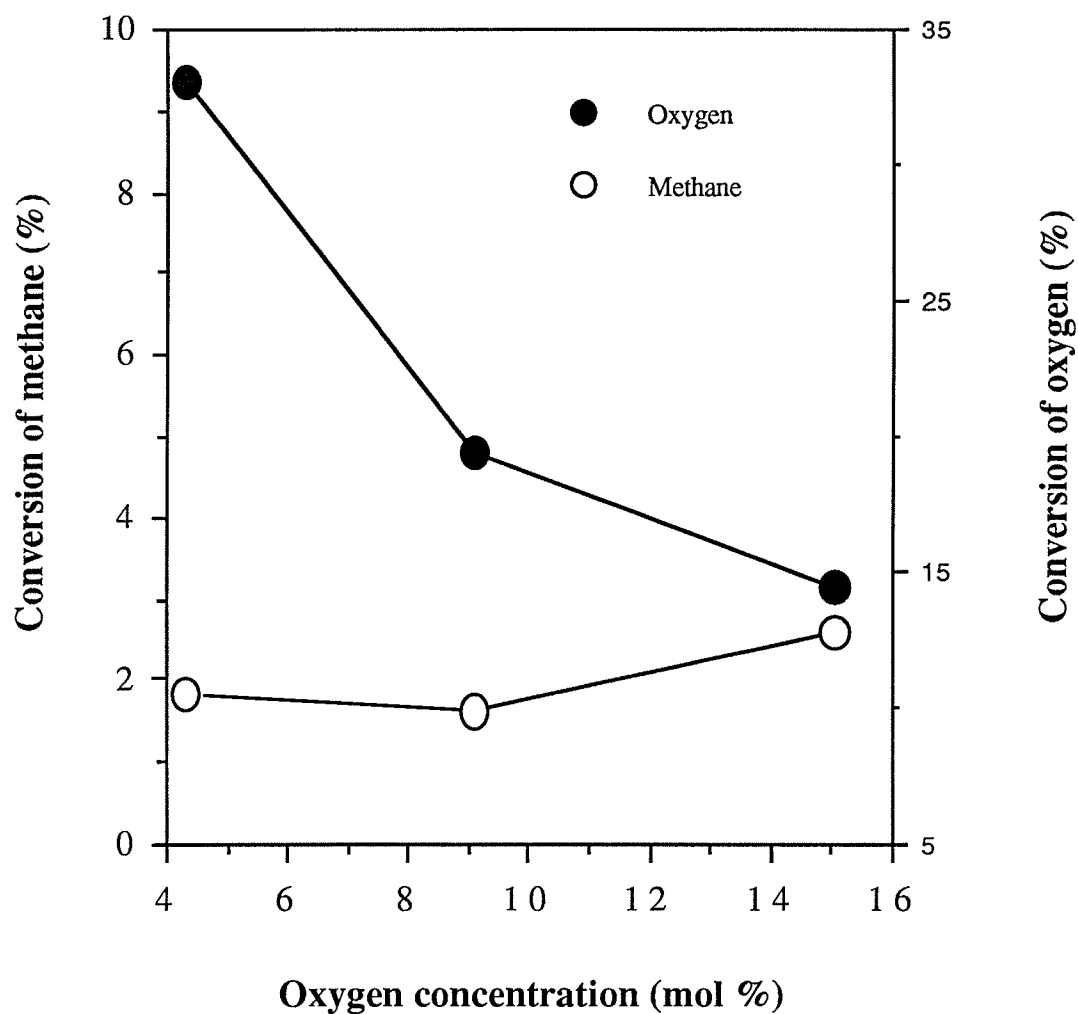


Figure 3.3-10. Variation of conversion with  $\text{O}_2$  concentration in the feed-gas

Reaction temperature: 402 °C

Reaction pressure: 1.45 - 1.50 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca 8 wt %

Residence time: 3.81 - 4.24 min.

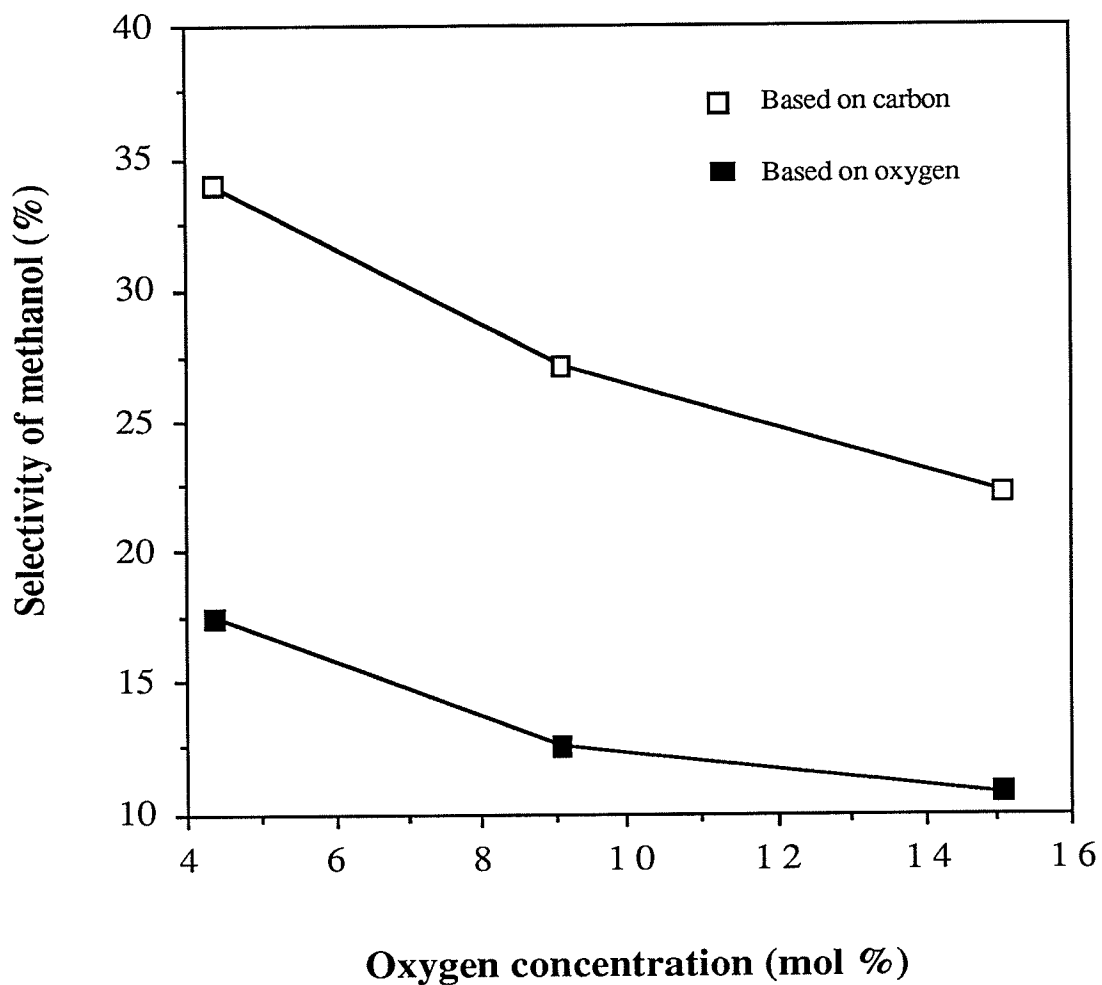


Figure 3.3-11. Variation of  $\text{CH}_3\text{OH}$  selectivity with  $\text{O}_2$  concentration in the feed-gas

Reaction temperature: 402 °C

Reaction pressure: 1.45 - 1.50 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca 8 wt %

Residence time: 3.81 - 4.24 min.

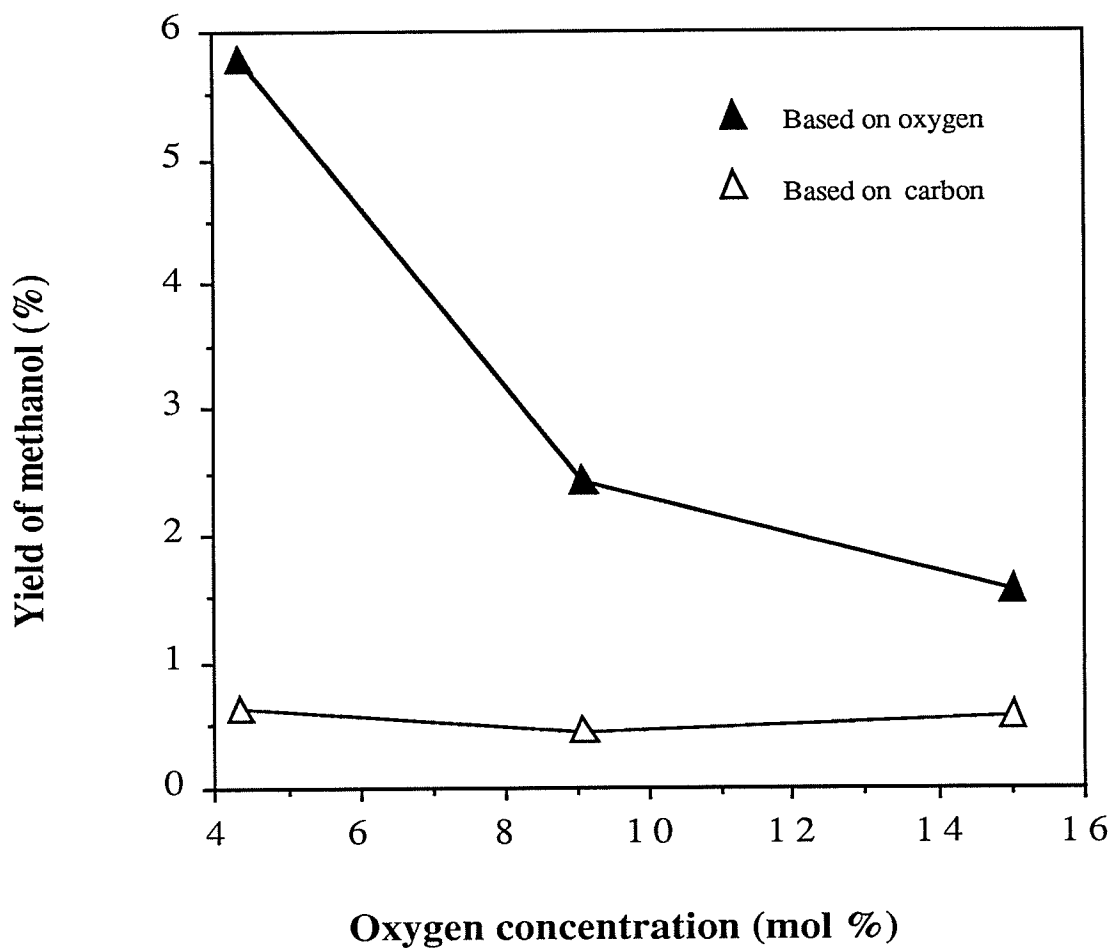


Figure 3.3-12. Variation of  $\text{CH}_3\text{OH}$  yield with  $\text{O}_2$  concentration in the feed-gas

Reaction temperature: 402 °C

Reaction pressure: 1.45 - 1.50 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca 8 wt %

Residence time: 3.81 - 4.24 min.

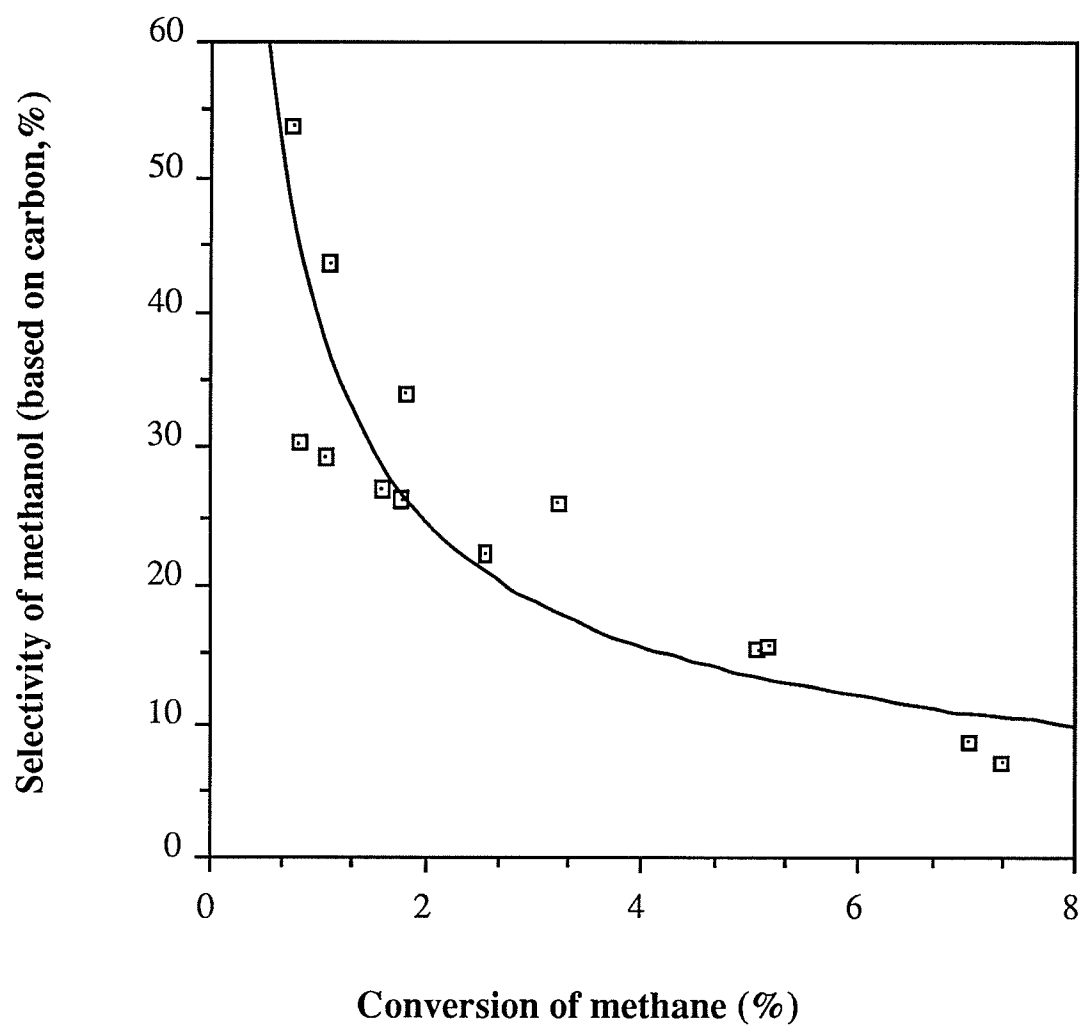


Figure 3.3-13. Variation of selectivity of methanol with conversion of methane



Table 3.3-4. Variation of the selectivity of methanol (based on carbon) with the conversion of methane

Experimental No.	CH <sub>4</sub> Conversion	CH <sub>3</sub> OH selectivity
32	0.827	30.3
33	1.09	29.3
34	1.78	26.3
35	5.07	15.4
36	7.34	6.99
37	7.00	8.59
38	5.16	15.6
39	3.23	25.9
40	1.11	43.6
50	2.56	22.2
52	1.61	27.1
56	1.83	34.0
80	0.773	53.8

## **PART II**

# **THE OZONE SENSITIZED ETHANE-OXYGEN REACTION**

### 3.4 Ozone sensitized ethane partial oxidation in Reaction System III

After the sensitization effects of ozone on the methane partial oxidation to methanol were confirmed and investigated, we began quantitatively to study the ozone sensitized partial oxidation of ethane.

It was found that, without ozone in the feed-gas, no reaction was observed even at reaction temperature of 282 °C (reaction pressure 1.35 atm and residence time 6.16 min. with 6.39 mol % O<sub>2</sub> in the feed) (experiment 63). However, with ozone in the feed, significant reaction between ethane and oxygen (conversions of oxygen and ethane were 18.3 % and 0.869 % (experiment 66), respectively) was detected at the reaction temperature of 252 °C and the other reaction conditions being almost the same as experiment 63. Under the reaction conditions similar to those of experiment 63, the conversion of oxygen and the conversion of ethane reached 58.2 % and 3.60 %, respectively, at a reaction temperature of 281 °C (experiment 65). The ozone-sensitized effect on the reaction of ethane with oxygen is clearly demonstrated in Table 3.4-1.

More comprehensive experiments were conducted to investigate the factors which influence the reaction between ethane and oxygen. The major products detected were water, formaldehyde, acetaldehyde, methanol, ethanol and carbon dioxide. Ethylene and carbon monoxide were also present in the products in almost all the experiments, except for the run at 252 °C. Methane appeared in the products in most of the runs. Small amounts of butane was detected in the experiments carried out at higher temperatures. Traces of formic acid was found in the products in some runs but, since its concentration was so low, it was not included in the mass balance calculation.

Table 3.4-1. Comparison of the conversions of the reactants with and without ozone in the feed-gas

Expt No.	Reaction condition					Conversion (mol %)	
	Temp (°C)	Press. (atm)	O <sub>2</sub> Conc in the feed (mol %)	RT * (min)	O <sub>3</sub> in O <sub>2</sub> (wt %)	C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>
63	282	1.35	6.39	6.16	0	0.00	0.00
66	252	1.35	6.59	6.06	~ 8	0.87	18.3
65	281	1.45	5.84	6.82	~ 8	3.60	58.2

\* RT = Residence time

The highest selectivities of methanol and ethanol obtained were 41.0 % and 21.8 % (based on carbon), respectively, the maximum ratio of the selectivity of ethanol to the selectivity of methanol was 0.76 (based on carbon, where the molar ratio of ethanol / methanol was 0.38), and the highest sum of the selectivities of formaldehyde, acetaldehyde, methanol, and ethanol (referred to as FAME) was 95.7 % (based on carbon). Although the selectivities of ethanol and methanol were not high, the selectivity of FAME was very high. Even when the conversion of ethane reached 3.6 %, the selectivity of FAME still achieved 89.3 % (based on carbon). Because formaldehyde, acetaldehyde, methanol, and ethanol are all valuable chemicals, this process seems economically practical.

#### 3.4.1. Effect of reaction temperature

The influence of reaction temperature on the ethane partial oxidation was investigated at residence times from 5.47 to 6.28 min., reaction pressures between 1.40

and 1.45 atm., and oxygen concentration in the feed from 5.24 to 5.71 mol % with about 8 wt % ozone in oxygen. Five runs (experiments 59, 60, 65, 71, and 72) were performed and the results obtained are presented in Appendix C.

The change of the concentrations of reactants in the output gas with reaction temperature is shown in Figure 3.4-1. The concentration of both ethane and oxygen in the output gas decreased with increase in reaction temperature. The concentration of oxygen decreased very rapidly from 4.14 to 0.14 % as the reaction temperature was increased from 267 to 300 °C, and then diminished to zero (complete consumption) while the reaction temperature was raised from 300 to 370 °C.

Figures 3.4-2a and 3.4-2b show the effect of the reaction temperature on the product composition. The concentration of water increased very rapidly with increase in reaction temperature up to 300 °C, and then increased slowly with further increase in temperature. For carbon monoxide, the concentration increased very slowly with increase in temperature in the range below 280 °C but increased very rapidly as the reaction temperature was raised from 280 to 310 °C. Ethylene began to be detected at 267 °C at very low concentration (0.024 %) and its concentration increased to 0.55 % at 370 °C. The concentration of carbon dioxide did not change significantly with reaction temperature and remained at about 0.5 %. Below 267 °C no methane was observed and its concentration increased very slightly as the reaction temperature was raised from 267 to 281 °C and then increased significantly with increase in reaction temperature above 281 °C. No butane was detected at below 281 °C and its concentration increased only slightly with increase in the reaction temperature from 280 to 370 °C and reached only 0.09 % at 370 °C. The concentration of formaldehyde seemed to have reached a maximum value at about 280 °C and decreased very slowly with increase in reaction temperature from 280 to 350 °C. There were maximum values for methanol, ethanol and acetaldehyde in the reaction temperature range studied, indicating that they were intermediate products in the oxidation sequence of ethane being oxidized to carbon monoxide and carbon dioxide. The output concentration of

methanol reached its highest value at about 300 °C, whereas ethanol and acetaldehyde reached their maximum values at near 280 °C.

### Conversion

The variation of the conversions of the reactants with reaction temperature is shown in Figure 3.4-3. The conversion of oxygen went up very rapidly (almost linearly) with increase in reaction temperature from 267 to 300 °C and then increased very slowly at the reaction temperature higher than 300 °C and was completely consumed at 370 °C. The conversion of ethane showed a similar trend.

### Selectivity

The change of the selectivities (based on carbon) of methanol, ethanol, formaldehyde, acetaldehyde, FAME, and carbon monoxide with the reaction temperature is presented in Figure 3.4-4a. The selectivity of methanol obtained was higher than that of ethanol and reached its highest value at about 280 °C. The selectivities of ethanol, formaldehyde, acetaldehyde and FAME increased as the reaction temperature was reduced. At reaction temperatures below 280°C the selectivity of FAME was over 90 %. The variation trend of the selectivity of formaldehyde with reaction temperature was almost the same as that of acetaldehyde, indicating that the majority of formaldehyde was probably produced by the same precursors ( $\text{CH}_3\text{CH}_2\text{OO}$  and  $\text{CH}_3\text{CH}_2\text{O}$ ) as acetaldehyde. Since the selectivity of acetaldehyde is parallel to that of ethanol at higher reaction temperatures, it is probable that the majority of acetaldehyde and ethanol are produced via the same active species which might be  $\text{CH}_3\text{CH}_2\text{O}$ .

It is very interesting to compare the trend of the selectivity of FAME with reaction temperature to that of carbon monoxide. The change of the selectivity of FAME with reaction temperature is almost inversely related to that of carbon monoxide, indicating that the reduction of selectivity of FAME with increase in reaction temperature was caused by

FAME being further oxidized to carbon monoxide. It is clearly demonstrated in Figure 3.4-4a that lower reaction temperature favors the formation of alcohol and the preservation of FAME.

Figure 3.4-4b shows the variation of the ratio of the selectivity of ethanol to the selectivity of methanol (E/M) as a function of the reaction temperature. Generally E/M increased as the reaction temperature was decreased, especially at below 300°C. Since ethanol is a more valuable chemical than methanol, the reaction temperature should be controlled at below 300°C from the viewpoint of economics.

### Yield

The effect of reaction temperature on the yields (based on carbon) of ethanol, methanol, and FAME is presented in Figure 3.4-5. All the yields passed through their maximum values in the range of the reaction temperature studied. The yields of ethanol and FAME reached their highest values at about 280°C and the yield of methanol reached its maximum value at a higher temperature (near 300 °C).

### **3.4.2. Effect of oxygen concentration in the feed-gas**

Three experiments (Experiments 65, 67, 68) were run to investigate the influence of oxygen concentration in the feed-gas on the reaction of ethane with oxygen at a reaction temperature of 281 °C, reaction pressure of 1.45 atm and residence times from 6.23 to 6.82 min with about 8 (wt) % ozone in oxygen. The results obtained are presented in Appendix C.

### Conversion

Figure 3.4-6 shows the variation of the conversion of ethane and the conversion of oxygen with increase in the oxygen concentration in the feed-gas. The conversion of oxygen decreased with the increase of oxygen concentration. In contrast, the conversion of ethane increased as the concentration of oxygen was increased.

Four factors might be responsible for the increase of the conversion of ethane with increase in oxygen concentration. (1) As the concentration of oxygen in the feed-gas increased, the probability of the collision between ethane and oxygen increased so that the number of moles of ethane reacted increased. (2) The rates of some elementary reactions in the reaction system were accelerated due to increase of oxygen concentration, causing the total rate of the reaction to increase so that the conversion of ethane increased. (3) The increase of oxygen concentration resulted in a slight decrease in the concentration of ethane in the feed-gas making the conversion value of ethane increase since the conversion is defined as

$$\text{conversion} = \frac{\text{number of moles reacted}}{\text{number of moles fed}}$$

(4) Since the concentration of  $\text{O}_3$  in the  $\text{O}_2$  was constant, an increase in the  $\text{O}_2$  concentration resulted in a higher concentration of O atom which initiated the reaction. The last factor probably played the most important part.

Since the concentration of oxygen was usually less than 10 %, the mole fraction of oxygen only accounted for a small part of the feed-gas. The number of the moles of oxygen reacted did not increase too much when the oxygen concentration was increased but the number of the moles of oxygen in the feed-gas increased considerably compared to the increase of the number of the moles of oxygen reacted so that the conversion of oxygen decreased with increase in oxygen concentration.

### Selectivity

The influence of oxygen concentration in the feed-gas on the selectivity is presented in Figure 3.4-7. The selectivity of ethanol was almost independent of the oxygen concentration. The selectivity of both methanol and formaldehyde diminished with increase in oxygen concentration in the feed-gas but decreased more in the oxygen concentration range from 6 to 10 % than in the range from 10 to 14 %. The selectivity of FAME



decreased as the oxygen concentration in the feed gas was increased from 6 to 10 % and, at the oxygen concentration higher than 10 %, the selectivity became almost independent of the oxygen concentration. The decrease of the selectivity of methanol and formaldehyde with increasing oxygen concentration was most probably attributed to the further oxidation of methanol and formaldehyde to carbon monoxide as demonstrated in Figure 3.4-7 by the opposite variation trend of the selectivity of carbon monoxide with oxygen concentration to those of ethanol and formaldehyde.

It is implied by the relationship between the selectivities of methanol and formaldehyde and oxygen concentration that molecular oxygen probably participated in some steps in the oxidation of formaldehyde and methanol to carbon monoxide.

The ratio of the selectivity of ethanol to the selectivity of methanol will be expected to increase as the oxygen concentration in feed-gas is raised since the selectivity of ethanol is almost independent of oxygen concentration but the selectivity of methanol decreases with increase of oxygen concentration in the feed (Figure 3.4-7).

### Yield

Although the selectivities of methanol and FAME decreased with increase in oxygen concentration and the selectivity of ethanol was independent of oxygen concentration, the yields of these products increased as the oxygen concentration was raised (Figure 3.4-8) due to the higher conversion of ethane (Figure 3.4-6). The maximum values were obtained at the highest oxygen concentration studied.

#### **3.4.3. Effect of residence time**

The influence of the residence time on the ozone-sensitized ethane oxidation was investigated at the reaction temperature of 281 °C, reaction pressures from 1.35-1.55 atm, oxygen concentrations in the feed-gas between 11.45 and 14.65 (mol) % with ~8 (wt) %

ozone in oxygen in the feed-gas. Three runs (Experiments 68, 69, and 70) were made and the results are presented in Appendix C.

### Conversion

The effect of residence time on the conversion of the reactants is shown in Figure 3.4-9. The conversion of ethane generally increased as the residence time was increased. The  $O_2$  concentration in the feed in Experiment 70 (residence time 9.52 min) was 11.45 mol % but in Experiment 68 (residence time 6.23 min.) was 13.96 mol %. If the  $O_2$  concentration in experiment 70 had been kept the same as that in Experiment 68, the conversion of the former might have been higher than that of the latter. The conversion of oxygen increased more quickly with increase of the residence time.

### Selectivity

Figure 3.4-10a shows the variation of selectivities of methanol, ethanol and FAME with residence time. All the selectivities decreased with increase in the residence time. The highest selectivities were obtained at the lowest residence time used. Further reduction of the residence time was limited by the back pressure from the sampling valves in both G.C.s.

The ratio of ethanol selectivity to methanol selectivity (E/M) as a function of the residence time is presented in Figure 3.4-10b. E/M decreased as the residence time was increased. However, it was observed by Gesser et al. that E/M increased with increase in the residence time in the direct conversion of ethane to ethanol by the homogeneous partial oxidation at high pressure<sup>43</sup>. There are two possible factors which might be responsible for these opposite trends of E/M with the residence time. (1) In their reaction system no sensitizer was used and an induction period probably was required for the partial oxidation of ethane to ethanol. Therefore a longer residence time favored the formation of ethanol. In the present reaction system the addition of ozone as a sensitizer into the reaction system

reduced or probably completely eliminated the induction period so that increasing the residence time caused a decrease in E/M due to ethanol being less stable than methanol at high temperatures. (2) The residence time used in this research were generally longer than that of Gesser et al. If the residence time in their system had been further increased, the E/M might have decreased. Nevertheless, the first explanation is probably the main factor causing the opposite trends of E/M with the residence time in these two different reaction systems.

### Yield

The yields of methanol, ethanol, and FAME passed through their maximum values in the residence time range studied (Figure 3.4-11). Ethanol and methanol reached their highest yields at ~6.3 min and ~7.2 min, respectively, whereas FAME reached its maximum value at ~6.8 min.

#### **3.4.4. Variation of the selectivities with the conversion of ethane**

Figure 3.4-12 shows the change in the selectivities of ethanol, methanol and FAME as a function of the conversion of ethane. The selectivities of both FAME and ethanol increased with the decrease in the conversion of ethane. The selectivity of FAME increased very rapidly from ~ 0 % to 86 % as the conversion of ethane was decreased from 7.1 % to 4 %. At the range of the conversion of ethane below 3 % further reducing the conversion of ethane only caused slight increase of the selectivity of FAME. In order to obtain high selectivity of FAME, the conversion of ethane should be controlled at below 4 %. For ethanol, the selectivity increased slowly as the conversion of ethane was decreased from 6.4 % to 4.6 %. Further decreasing the conversion from 4.6 % to 2.0 % only resulted in a very slight increase in the selectivity. At the conversion of ethane below 2 % the selectivity of ethanol increased more quickly with decrease in the conversion of ethane. The selectivity of methanol passed through its maximum value at ~4 % for the conversion of

ethane.

### 3.4.5 Variation of the yields with the conversion of ethane

The change of the yield of ethanol, methanol and FAME with the conversion of ethane is presented in Figure 3.4-13. The three yields passed through maximum values in the range of the conversion studied. The ethanol reached its highest value at the conversion of ~4.4 %, whereas the FAME and methanol reached their maximum values at the conversion of ~4.7 %. It is interesting to note that they reached the maximum values at almost the same level of the conversion of ethane.

### 3.4.6. Effect of the ozone concentration in oxygen

In order to determine the minimum ozone concentration at which its effect could be observed, the influence of ozone concentration on the conversion of ethane was investigated by changing the voltage charged on the generator. The results obtained are presented in Table 3.4-1.

It was found that the conversion of ethane increased with increase in the voltage charged on the generator, i.e., with increase in ozone concentration (Table 3.4-1) at the reaction temperature of 280 °C, residence time in the reactor of ~6 min. and O<sub>2</sub> concentration in the feed gas of ~9 %. With ~1 % O<sub>3</sub> in O<sub>2</sub> considerable conversion of ethane was observed compared to no reaction being detected without O<sub>3</sub> in O<sub>2</sub>. It is clear that the minimum ozone concentration at which the effect of ozone sensitization could be observed is somewhat less than 1 (wt) %. The results also suggests that there is a possibility that the reaction of ethane with oxygen can be initiated by O<sub>3</sub> at a slightly higher pressure if the concentration of ozone generated in oxygen can reach over 1 %.

Table 3.4-2 Effect of ozone concentration on the ethane conversion

Exp. No.	Pressure in the generator (atm)	Voltage on the primary of the high voltage transformer (V)	O <sub>3</sub> wt %	C <sub>2</sub> H <sub>6</sub> conversion (%)
73	1.60	61.5		very little
76	1.60	72.0		2.03
86	1.60	72.2	1.0	

### 3.4.7. Mass balance

#### (a) Expressions for calculation of conversion, selectivity and yield

The conversions of ethane and oxygen, selectivities of ethanol, methanol and other products, and yields of products were calculated by using the following overall expressions:

$$\text{C}_2\text{H}_6 \text{ conversion (mol \%)} = \frac{\sum \text{C products}}{2 \times \text{C}_2\text{H}_{6\text{out}} + \sum \text{C products}} \times 100$$

$$\text{where } \sum \text{C products} = \text{CO} + (\text{CO}_2 - \text{CO}_{2(\text{in})} \frac{n_{\text{total (in)}}}{n_{\text{total (out)}}}) + \text{HCHO} + \text{CH}_3\text{OH} + 2 \times \text{CH}_3\text{CHO} + 2 \times \text{C}_2\text{H}_5\text{OH} + \text{CH}_4 + 2 \times \text{C}_2\text{H}_4 + 4 \times \text{C}_4\text{H}_{10}$$

and CO, CO<sub>2</sub>, HCHO, CH<sub>3</sub>OH, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>10</sub> and C<sub>2</sub>H<sub>6out</sub> refer to the mole percentages of these compounds in the exit stream from the reactor, and CO<sub>2(in)</sub> and n represent the mole percentage of carbon dioxide in the feed-gas and the number of moles, respectively.

$$\text{O}_2 \text{ conversion (mol \%)} = \frac{\sum \text{O products}}{2 \times \text{O}_{2\text{out}} + \sum \text{O products}} \times 100$$

$$\text{where } \sum \text{O products} = \text{CO} + 2 \times (\text{CO}_2 - \text{CO}_{2(\text{in})} \frac{n_{\text{total (in)}}}{n_{\text{total (out)}}}) + \text{HCHO} + \text{CH}_3\text{OH} + \\ \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$$

and CO, CO<sub>2</sub>, HCHO, CH<sub>3</sub>OH, CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O and O<sub>2out</sub> refer to the mole percentages of these compounds in the exit stream from the reactor, and CO<sub>2(in)</sub> and n represent the mole percentage of carbon dioxide in the feed-gas and the number of moles, respectively.

$$\text{C}_2\text{H}_5\text{OH selectivity (based on carbon, mol \%)} = \frac{2 \times \text{C}_2\text{H}_5\text{OH}}{\sum \text{C products}} \times 100$$

$$\text{C}_2\text{H}_5\text{OH selectivity (based on oxygen, mol \%)} = \frac{\text{C}_2\text{H}_5\text{OH}}{\sum \text{O products}} \times 100$$

On a similar basis, all the selectivity of the other products were calculated.

$$\text{C}_2\text{H}_5\text{OH yield (based on carbon, mol \%)} =$$

$$\frac{\text{C}_2\text{H}_5\text{OH selectivity (based on carbon, mol \%)} \times \text{C}_2\text{H}_6 \text{ conversion (mol \%)}}{100},$$

$$\text{C}_2\text{H}_5\text{OH yield (based on oxygen, mol \%)} =$$

$$\frac{\text{C}_2\text{H}_5\text{OH selectivity (based on oxygen, mol \%)} \times \text{O}_2 \text{ conversion (mol \%)}}{100}$$

All the yields of the other products were calculated on a similar basis.

The calculation results of the conversions, selectivities and yields for each experiment are given in Appendix C.

The observations that the selectivity of ethanol based on carbon was always higher than that based on oxygen and that the conversion of oxygen was higher than the conversion of ethane can be explained by similar reasons to those presented in the section of the ozone sensitized partial oxidation of methane to methanol in this thesis.

#### (b) Expression for the calculation of residence time

The residence time in the reactor was calculated by the expression

$$\text{Residence time} = \frac{V_{\text{reactor}} P_{\text{rxn}} T_{\text{room}}}{F_{\text{in}} P_{\text{atm}} T_{\text{rxn}}}$$

where  $F_{\text{in}}$  represents the flow rate of the feed-gas at room temperature and atmospheric pressure, and the subscript rxn refers to reaction.

#### (c) Equations for the calculation of the material balances of carbon, oxygen and hydrogen

Based on the assumption that the total mass of all the compounds entering the reactor was equal to the total mass of all the compounds leaving the reactor, material balances for carbon, oxygen and hydrogen were arrived at as follows:

$$\begin{aligned} \text{Since } \sum M_{i, \text{ in }} Y_{i, \text{ in }} n_{\text{total, in}} &= \sum M_{i, \text{ out }} Y_{i, \text{ out }} n_{\text{total, out}} \\ n_{\text{total, out}} &= \sum M_{i, \text{ in }} Y_{i, \text{ in }} n_{\text{total, in}} / \sum M_{i, \text{ out }} Y_{i, \text{ out}} \end{aligned}$$

where  $n$  and  $Y$  refer to the number of moles and the mole fraction, respectively, and  $M$  here represents the molar mass.

$Y_i$  was obtained from the results of analysis and  $n_{\text{total, in}}$  was calculated from the equation

$$n_{\text{total, in}} = \frac{F_{\text{in}} P_{\text{atm}}}{RT_{\text{room}}}$$

where  $F_{\text{in}}$  refers to the total flow rate of the feed-gas at room temperature and atmospheric pressure.

Then the moles of the reactants and products in a unit of time were calculated by the two equations

$$n_{i, \text{in}} = Y_{i, \text{in}} n_{\text{total, in}}$$

and

$$n_{i, \text{out}} = Y_{i, \text{out}} n_{\text{total, out.}}$$

And the mass balances were calculated by

$$\frac{M_{\text{C}_{\text{out}}}}{M_{\text{C}_{\text{in}}}} = \frac{n_{\text{C}_{\text{out}}}}{n_{\text{C}_{\text{in}}}} = \frac{2 \times n_{\text{C}_2\text{H}_{6\text{out}}} + \sum \text{C products}}{2 \times n_{\text{C}_2\text{H}_{6\text{in}}} + n_{\text{CO}_{2\text{in}}}}$$

where M here means mass and

$$\sum \text{C products} = n_{\text{CO}} + n_{\text{CO}_2} + n_{\text{HCHO}} + n_{\text{CH}_3\text{OH}} + 2 \times n_{\text{CH}_3\text{CHO}} + \\ 2 \times n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{CH}_4} + 2 \times n_{\text{C}_2\text{H}_4} + 4 \times n_{\text{C}_4\text{H}_{10}}$$

$$\frac{M_{\text{O}_{\text{out}}}}{M_{\text{O}_{\text{in}}}} = \frac{n_{\text{O}_{\text{out}}}}{n_{\text{O}_{\text{in}}}} = \frac{2 \times n_{\text{O}_{2\text{out}}} + \sum \text{O products}}{2 \times n_{\text{O}_{2\text{in}}} + 2 \times n_{\text{CO}_{2\text{in}}}}$$

$$\text{where } \sum \text{O products} = n_{\text{CO}} + 2 \times n_{\text{CO}_2} + n_{\text{HCHO}} + n_{\text{CH}_3\text{OH}} + n_{\text{CH}_3\text{CHO}} + \\ n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{H}_2\text{O}}$$

$$\frac{M_{\text{H}_{\text{out}}}}{M_{\text{H}_{\text{in}}}} = \frac{n_{\text{H}_{\text{out}}}}{n_{\text{H}_{\text{in}}}} = \frac{6 \times n_{\text{C}_2\text{H}_{6\text{out}}} + \sum \text{H products}}{6 \times n_{\text{C}_2\text{H}_{6\text{in}}}}$$

$$\text{where } \sum \text{H products} = 2 \times n_{\text{H}_2\text{O}} + 2 \times n_{\text{HCHO}} + 4 \times n_{\text{CH}_3\text{OH}} + 4 \times n_{\text{CH}_3\text{CHO}} + \\ 6 \times n_{\text{C}_2\text{H}_5\text{OH}} + 4 \times n_{\text{CH}_4} + 4 \times n_{\text{C}_2\text{H}_4} + 10 \times n_{\text{C}_4\text{H}_{10}}$$



The calculation of the material balances, based on total mass balance, was performed for each experiments (Appendix C). Both an average of the ratio of Mass(out) to Mass (in) and a standard deviation were obtained for carbon, oxygen and hydrogen, and the results are provided below.

$$\frac{M_{C_{out}}}{M_{C_{in}}} = 0.990 \pm 0.009$$

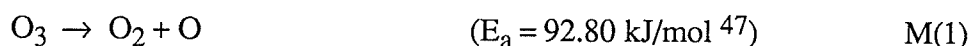
$$\frac{M_{O_{out}}}{M_{O_{in}}} = 1.094 \pm 0.088$$

$$\frac{M_{H_{out}}}{M_{H_{in}}} = 0.993 \pm 0.007$$

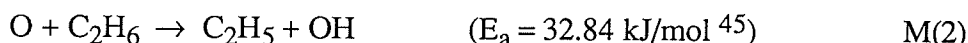
### 3.4.8. Reaction mechanism

#### (a) At lower reaction temperatures

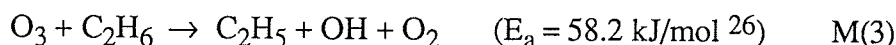
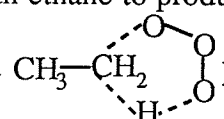
Since no reaction between ethane and oxygen was observed at lower reaction temperatures without ozone in the feed-gas but considerable reaction was detected at the same temperature with ozone in the feed-gas, it is clearly demonstrated that the reaction between ethane and dioxygen was initiated by ozone. The first step was that ozone decomposed to dioxygen and an oxygen atom



then, the oxygen atom reacted with ethane to generate an ethyl free radical.



Perhaps some undecomposed ozone directly reacted with ethane to produce an ethyl free radical (possibly via a five member ring intermediate state  $CH_3-CH_2$



and then the reaction proceeded by a free radical chain reaction mechanism. The following

reactions are believed to occur.

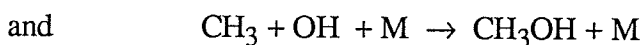
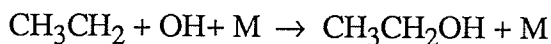
	$E_a$ (kJ/mol)	
$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	7.57 <sup>47</sup>	M(4)
$C_2H_5 + O_2 \rightarrow C_2H_5OO$	0 <sup>48</sup>	M(5)
$C_2H_5 + O_2 \rightarrow C_2H_4 + HOO$	16.21 <sup>7</sup>	M(6)
$C_2H_5OO + C_2H_6 \rightarrow C_2H_5OOH + C_2H_5$		M(7)
$CH_3CH_2OOH \rightarrow CH_3CH_2O + OH$	158 <sup>50</sup>	M(8)
$C_2H_5O + C_2H_6 \rightarrow C_2H_5OH + C_2H_5$	29.3 <sup>44</sup>	M(9)
$CH_3CH_2OO \rightarrow CH_3CHO + OH$		M(10)
$CH_3CH_2OO \rightarrow CH_3O + HCHO$	90.4 <sup>49</sup>	M(11)
$HCHO + OH \rightarrow CHO + H_2O$	0.711 <sup>47</sup>	M(12)
$CH_3CH_2O \rightarrow CH_3CHO + H$	97.7 <sup>49</sup>	M(13)
$CH_3CHO + OH \rightarrow CH_3CO + H_2O$	0.00 <sup>47</sup>	M(14)
$CH_3CO \rightarrow CH_3 + CO$	72.13 <sup>47</sup>	M(15)
$CHO + C_2H_6 \rightarrow HCHO + C_2H_5$	76.29 <sup>7</sup>	M(16)
$CH_3CH_2O \rightarrow CH_3 + HCHO$	92.5 <sup>44</sup>	M(17)
$CH_3 + O_2 \rightarrow CH_3OO$	0 <sup>7</sup>	M(18)
$CH_3OO + C_2H_6 \rightarrow CH_3OOH + C_2H_5$	62.52 <sup>7</sup>	M(19)
$CH_3OOH \rightarrow CH_3O + OH$	161 <sup>50</sup>	M(20)
$CH_3O + C_2H_6 \rightarrow CH_3OH + C_2H_5$	29.68 <sup>7</sup>	M(21)
$CH_3O \rightarrow HCHO + H$	88.07 <sup>47</sup>	M(22)
$CH_3OO \rightarrow HCHO + OH$		M(23)
$CHO + O_2 \rightarrow CO + HOO$	7.067 <sup>7</sup>	M(24)
$CHO + OH \rightarrow HCOOH$		M(25)
$CHO + OH \rightarrow CO + H_2O$	0 <sup>7</sup>	M(26)
$CH_2O + CH_3 \rightarrow CH_4 + CHO$	24.53 <sup>7</sup>	M(27)
$CHO + CH_3 \rightarrow CH_4 + CO$	0.00 <sup>47</sup>	M(28)



etc.

Ethanol is produced by Reaction M(9). Reactions M(10) and M(13) account for the formation of acetaldehyde. Although formaldehyde could be produced by Reactions M(11), M(16), M(17), M(22) and M(23), the majority of formaldehyde was probably produced by Reaction M(11) and M(17), suggested by the observation that the selectivity trend of formaldehyde with reaction temperature was parallel to that of acetaldehyde (Figure 3.4-4a). Methane could be generated by Reactions M(27), M(28) and M(29), and ethylene by Reactions M(6), M(30), and M(31). Reaction M(25) might be responsible for the formation of traces of formic acid.

The reactions



were proposed to occur at high pressure <sup>43, 46</sup>. We believe that they may also occur at atmospheric pressure and contributed to some of the formation of ethanol and methanol.

Methanol could be produced from  $\text{CH}_3\text{CH}_2\text{OO}$  via the sequence of Reaction M(11) and Reaction M(21) and the rate controlling step was Reaction M(11) whose activation energy was 90.4 kJ/mol. Ethanol was produced from  $\text{CH}_3\text{CH}_2\text{OO}$  via the sequence of Reaction M(7), Reaction M(8) and Reaction M(9). Since the activation energy of Reaction M(7) should be close to the activation energy of Reaction M(19), i. e., 62.52 kJ/mol, the rate controlling step for the formation of ethanol from  $\text{CH}_3\text{CH}_2\text{OO}$  was Reaction M(8) whose activation energy was 158 kJ/mol. Therefore, the activation energy for the formation of ethanol was much higher than that for the formation of methanol from  $\text{CH}_3\text{CH}_2\text{OO}$ . This probably resulted in the observation that the selectivity of ethanol was lower than that of methanol.

## (b) At higher reaction temperatures

Whether ozone existed in the feed-gas or not, the reaction between ethane and oxygen was detected at higher reaction temperatures, but ozone accelerated the reaction. It is therefore reasonable to assume that the reaction of ethane with oxygen proceeded via both oxygen atom initiated reaction and ordinary homogeneous reaction at the higher temperatures.

In addition to Reactions from M(1) to M(31), the following additional reactions probably occurred at higher temperature.



Reaction M(32) is considered as the initial step for the ordinary homogeneous reaction and Reactions M(33) accounts for butane observed at the higher temperatures.

Since the ratio of the recombination reaction M(33) to the disproportionation reaction M(31) is independent of reaction temperature and since at lower temperature ethylene was detected but no butane was observed, this indicates that the ethylene observed at lower temperature was not produced by the disproportionation reaction, but by other reactions, for example, Reactions M(6) and M(30).

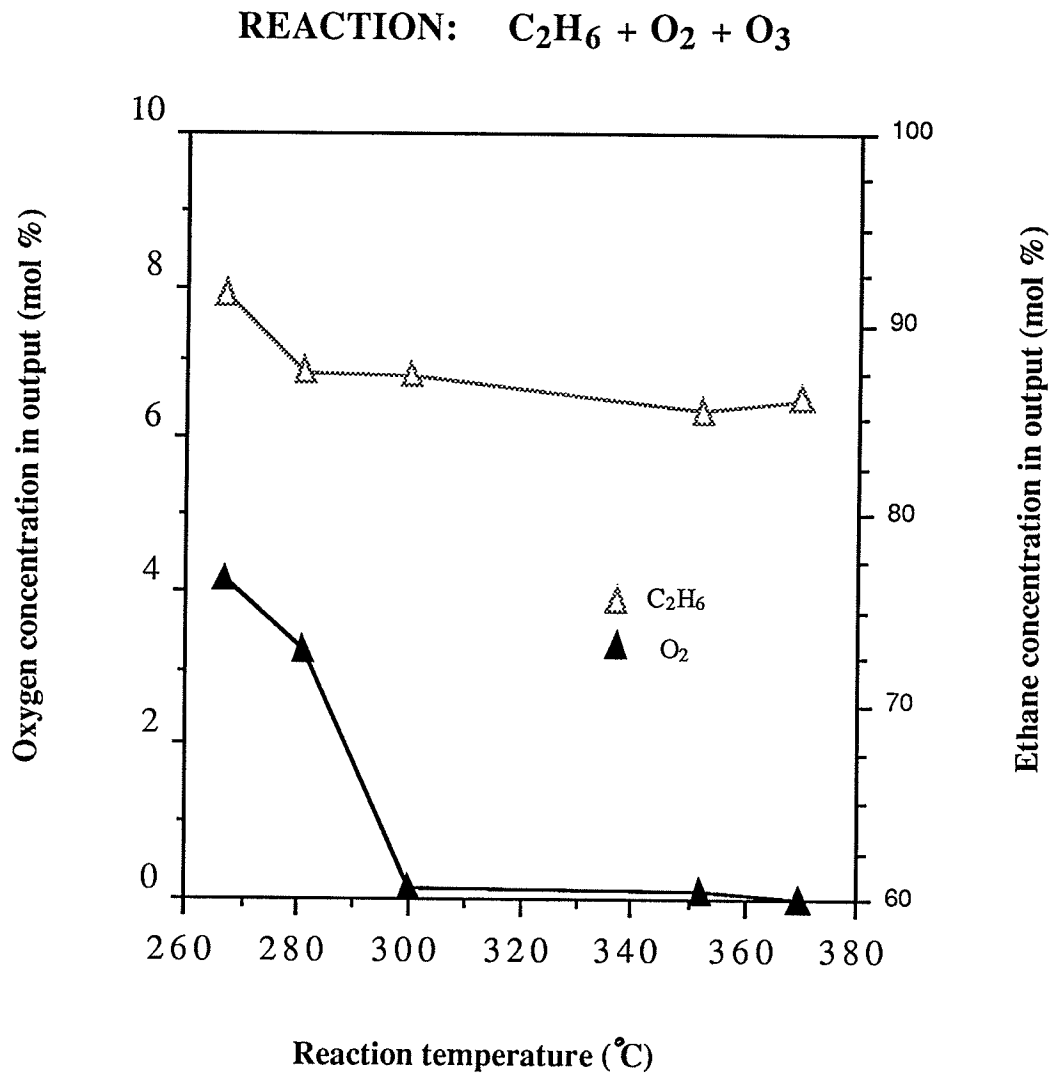


Figure 3.4-1. Variation of reactant concentration with reaction temperature

S.V.: 6.29-6.92  $\text{hr}^{-1}$  (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in feed-gas: 5.24-5.71 (mol)%

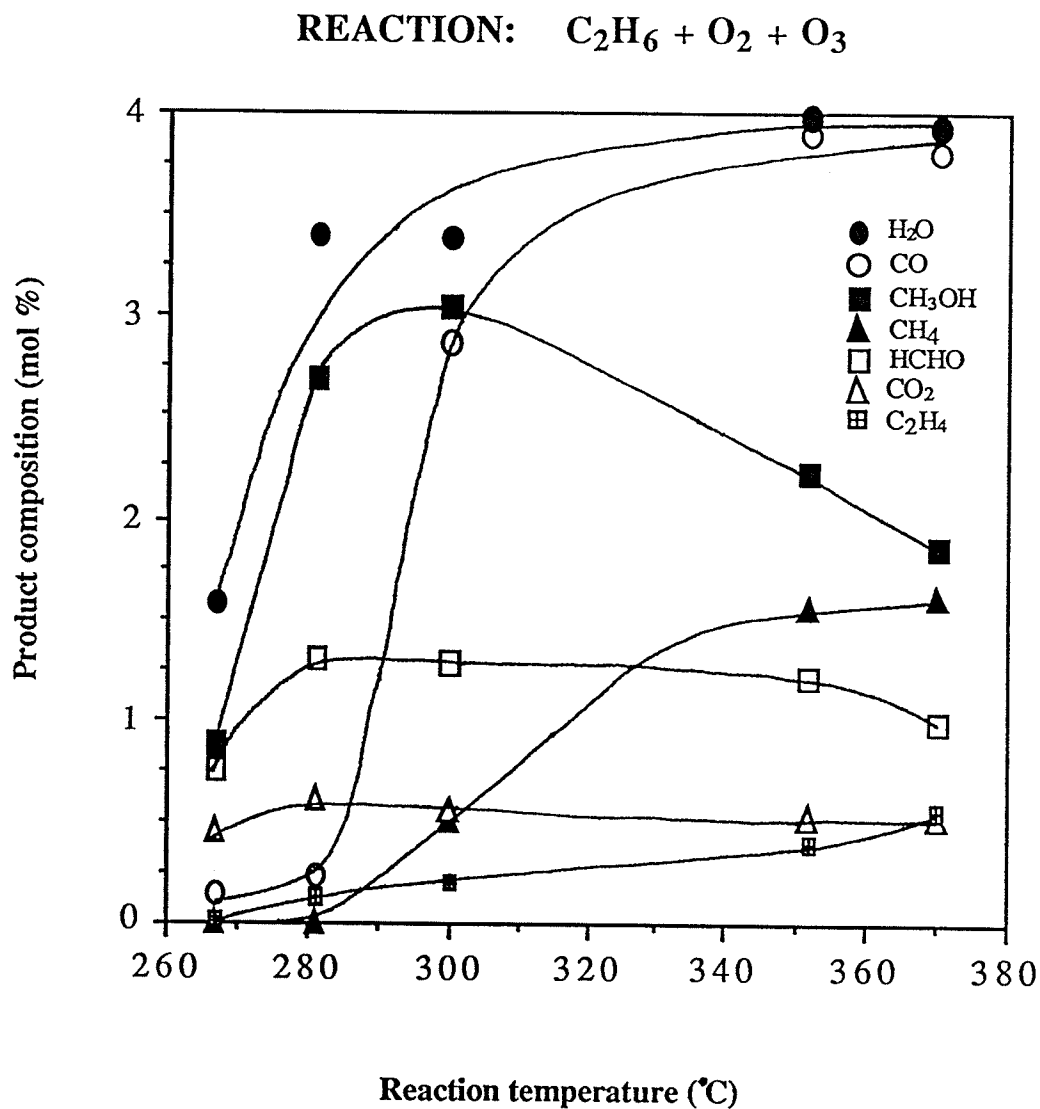


Figure 3.4-2a. Variation of product concentration with reaction temperature

S.V.: 6.29-6.92  $hr^{-1}$  (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

$O_3$  concentration in  $O_2$ : ca. 8 (wt)%

$O_2$  concentration in feed-gas: 5.24-5.71 (mol)%

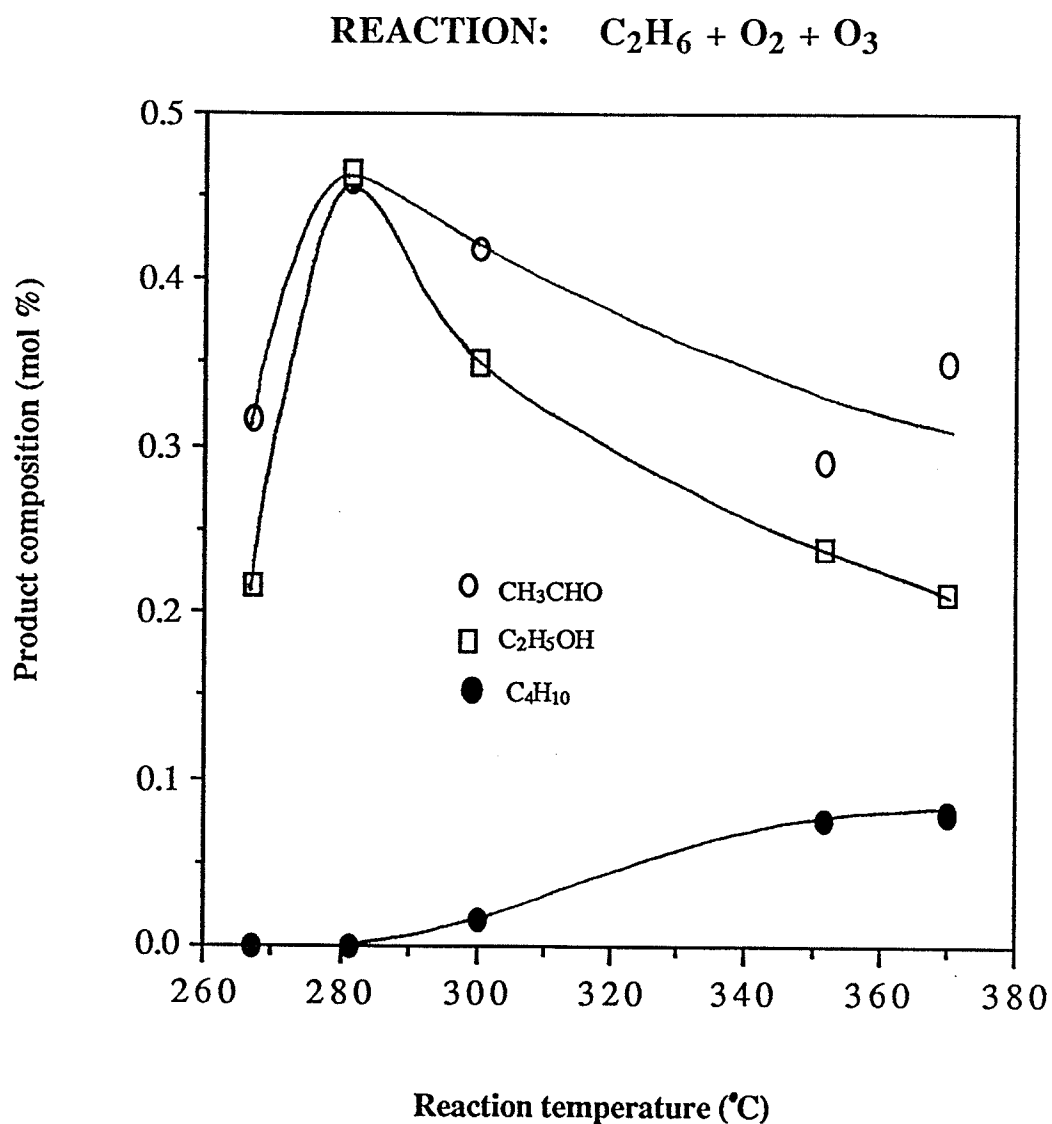


Figure 3.4-2b. Variation of product concentration with reaction temperature

S.V.: 6.29-6.92  $\text{hr}^{-1}$  (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in feed-gas: 5.24-5.71 (mol)%

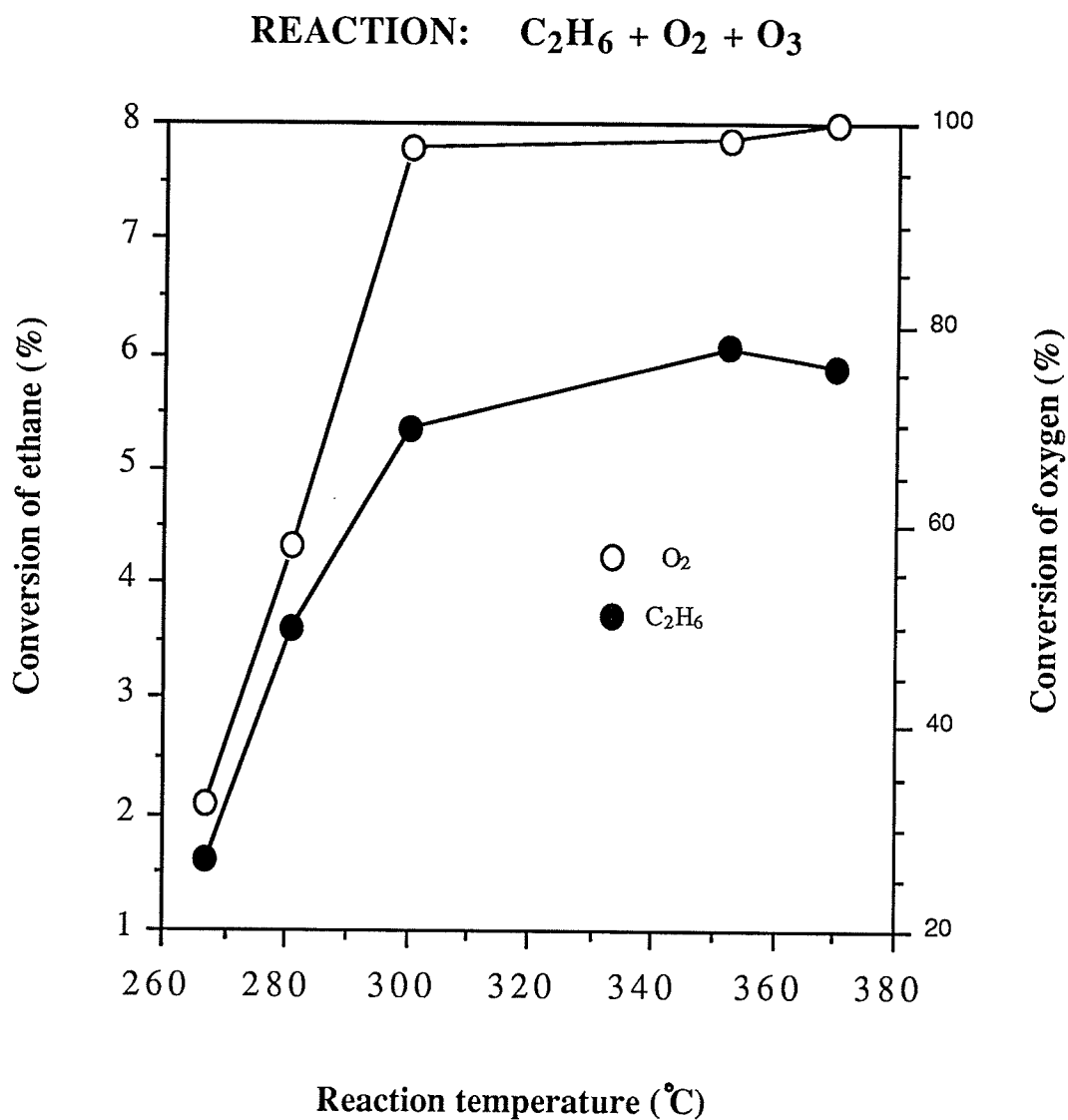


Figure 3.4-3. Variation of conversion with reaction temperature

S.V.: 6.29-6.92  $\text{hr}^{-1}$  (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in feed-gas: 5.24-5.71 (mol)%



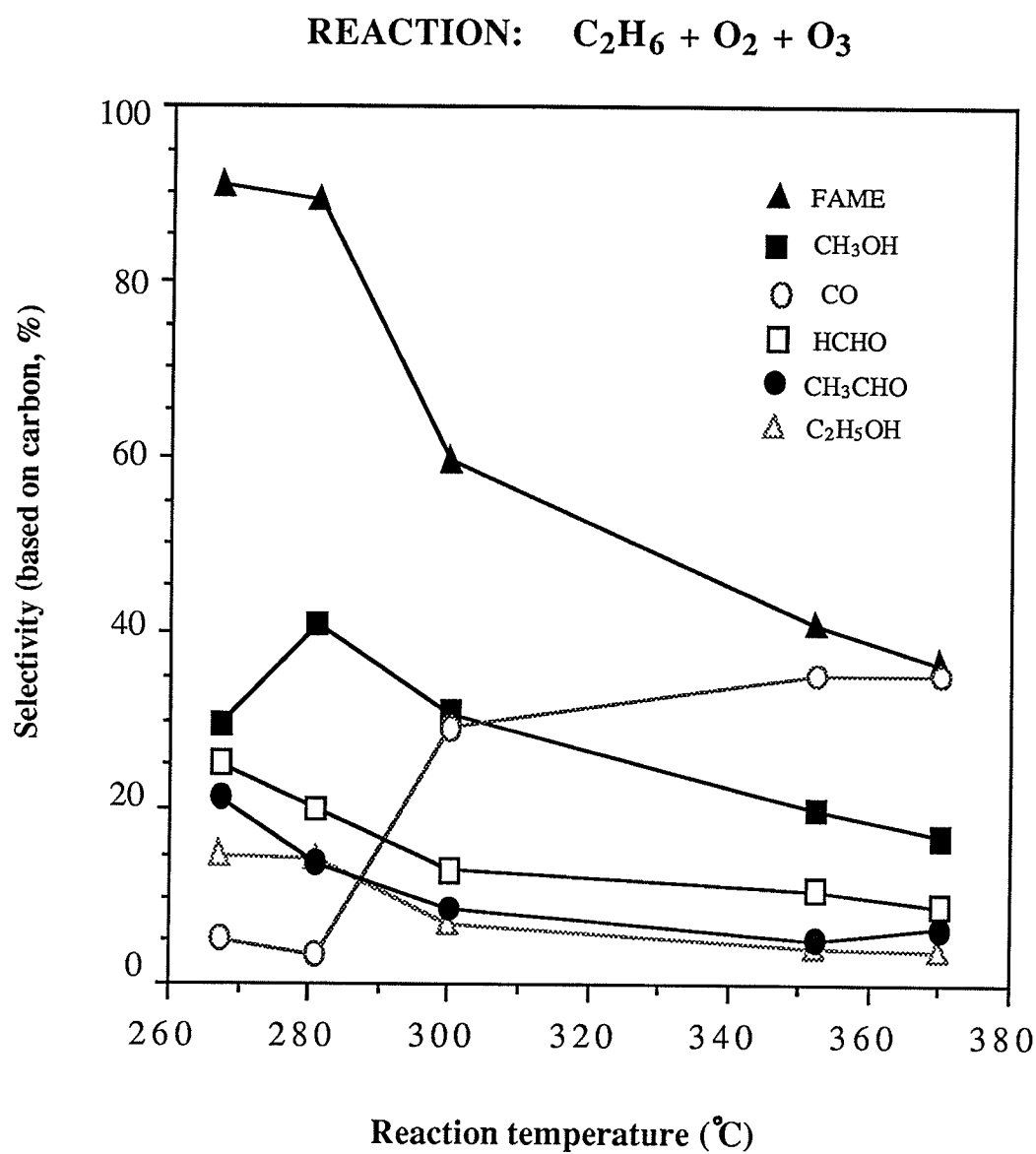


Figure 3.4-4a. Variation of selectivity with reaction temperature

S.V.: 6.29-6.92 hr<sup>-1</sup> (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in feed-gas: 5.24-5.71 (mol)%

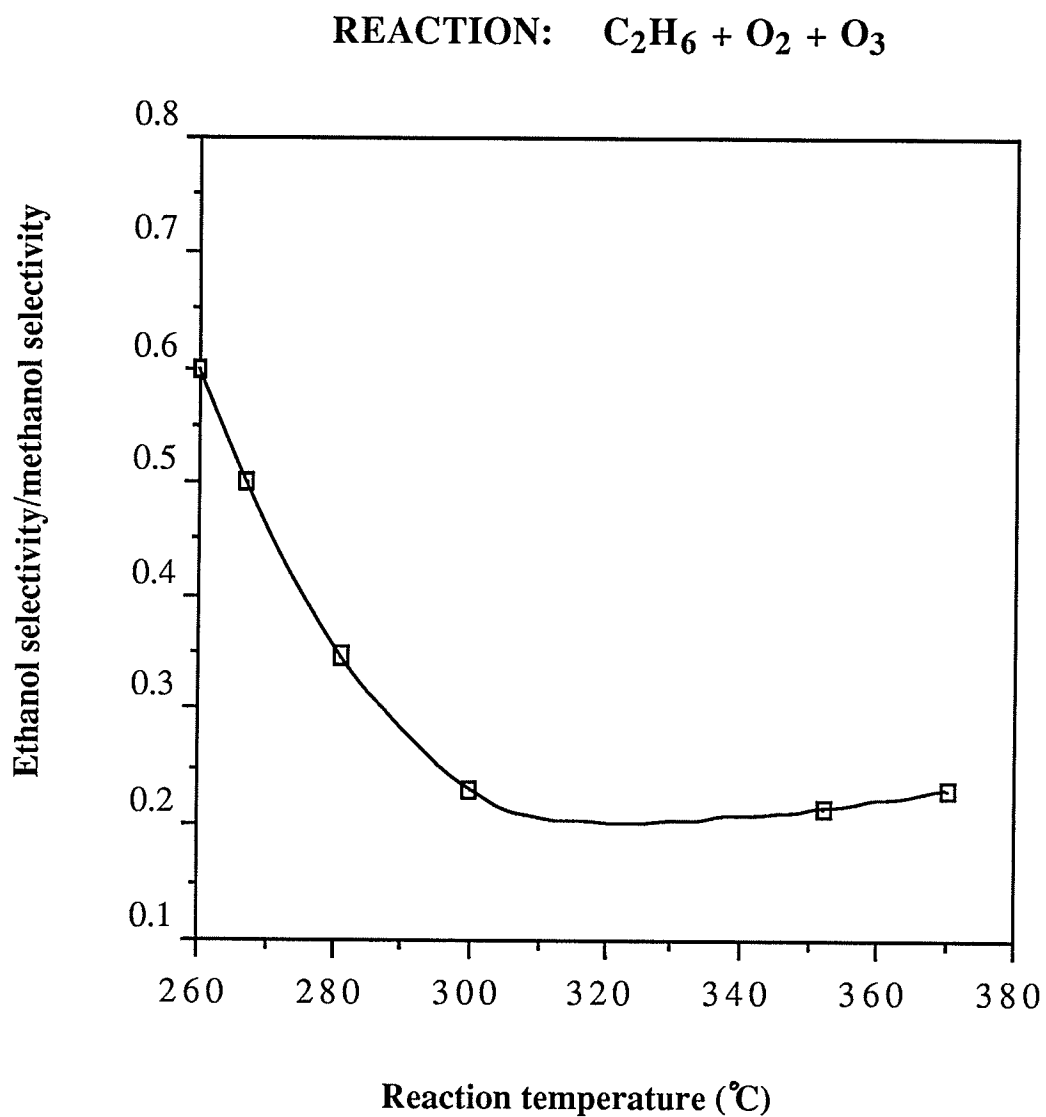


Figure 3.4-4b. Ethanol/methanol ratio as a function of reaction temperature

S.V.: 6.29-6.92  $\text{hr}^{-1}$  (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in feed-gas: 5.24-5.71 (mol)%

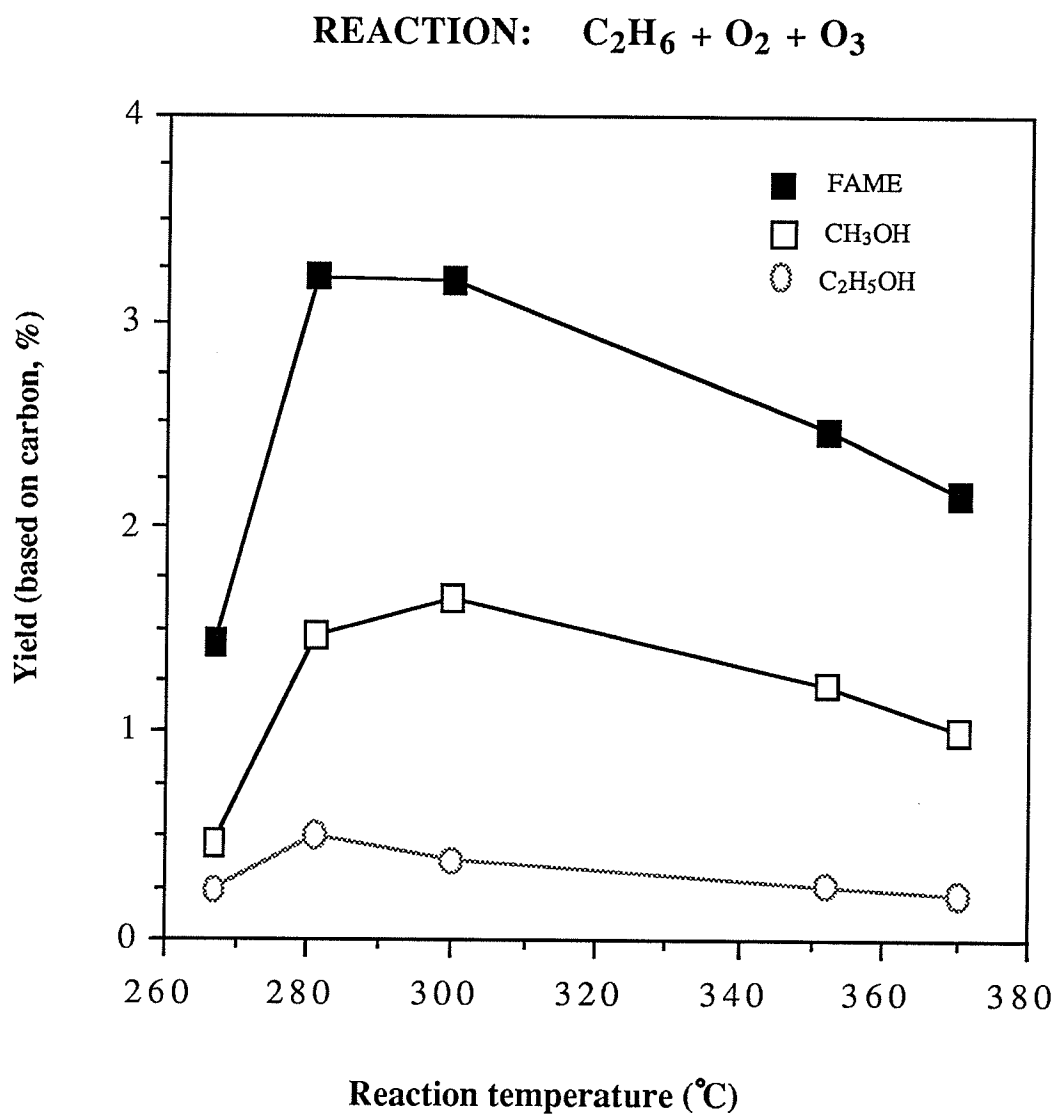


Figure 3.4-5. Variation of yield with reaction temperature

S.V.: 6.29-6.92 hr<sup>-1</sup> (STP)

Residence time: 5.47-6.82 min.

Reaction pressure: 1.4-1.45 atm

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in feed-gas: 5.24-5.71 (mol)%

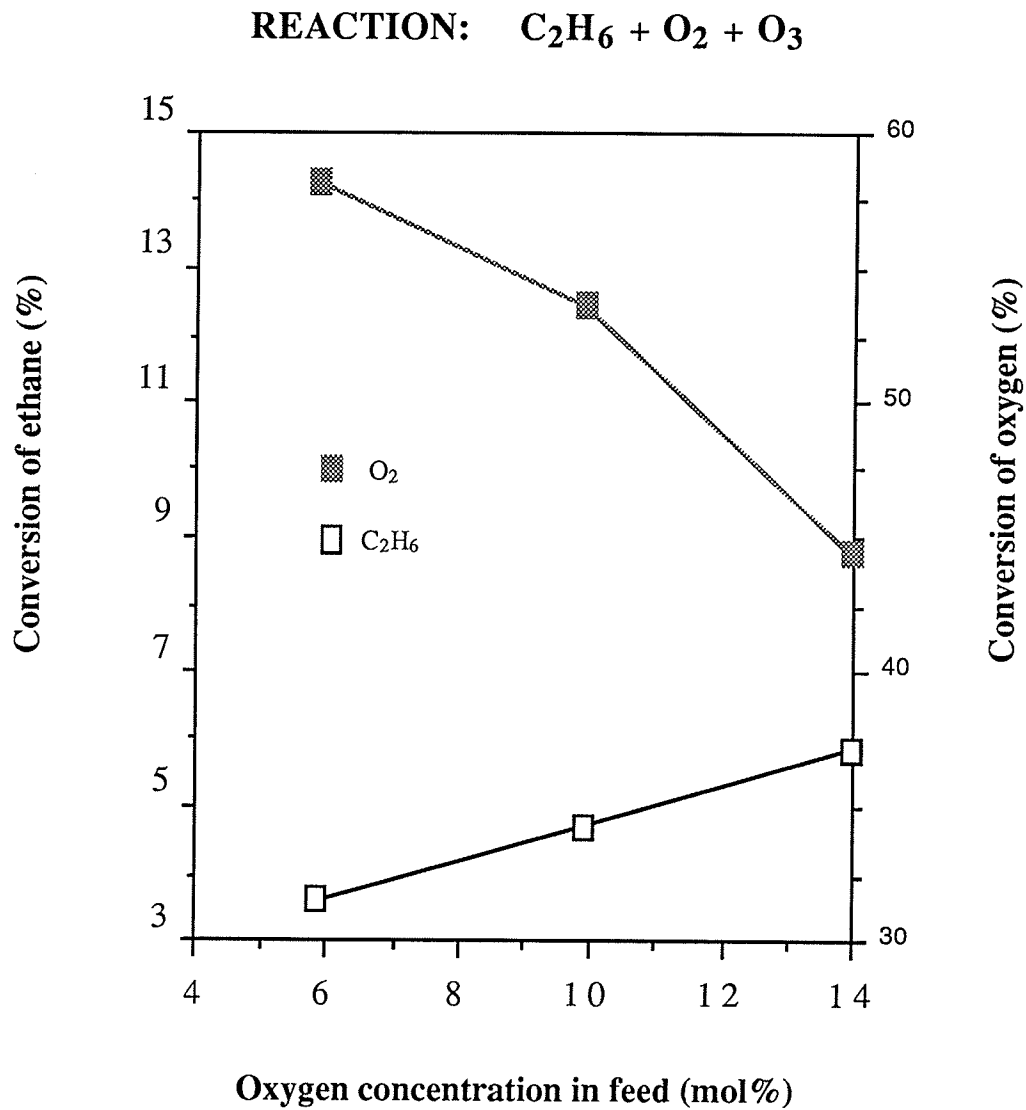


Figure 3.4-6. Variation of conversion with  $\text{O}_2$  concentration in the feed

Residence time: 6.23-6.82 min.

S.V.: 6.29-6.89  $\text{hr}^{-1}$  (STP)

Reaction pressure: 1.45 atm

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

Reaction temperature: 281  $^{\circ}\text{C}$

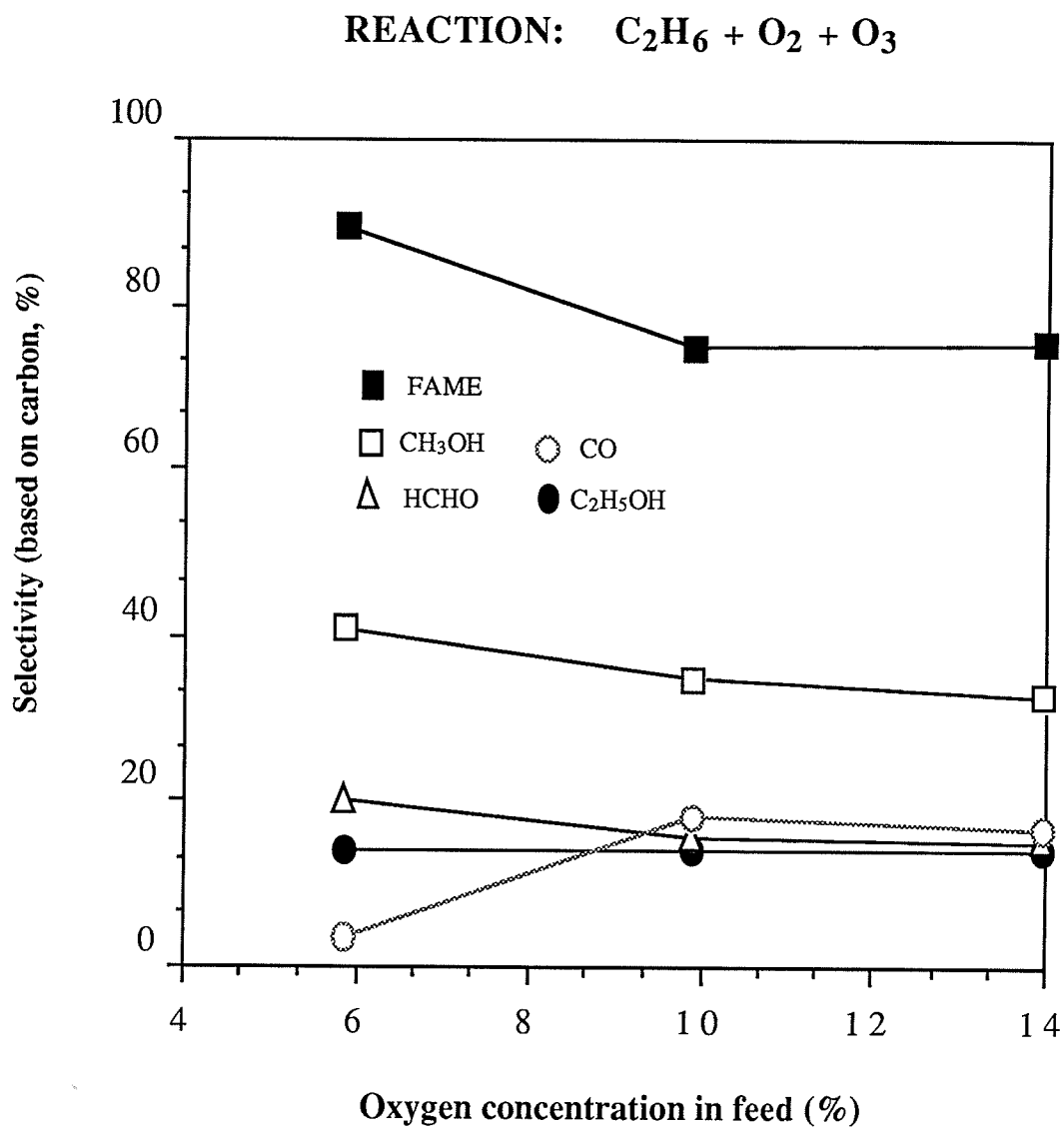


Figure 3.4-7. Variation of selectivity with  $O_2$  concentration in the feed

Residence time: 6.23-6.82 min.

S.V.: 6.29-6.89  $hr^{-1}$  (STP)

Reaction pressure: 1.45 atm

$O_3$  concentration in  $O_2$ : ca. 8 (wt)%

Reaction temperature: 281 °C

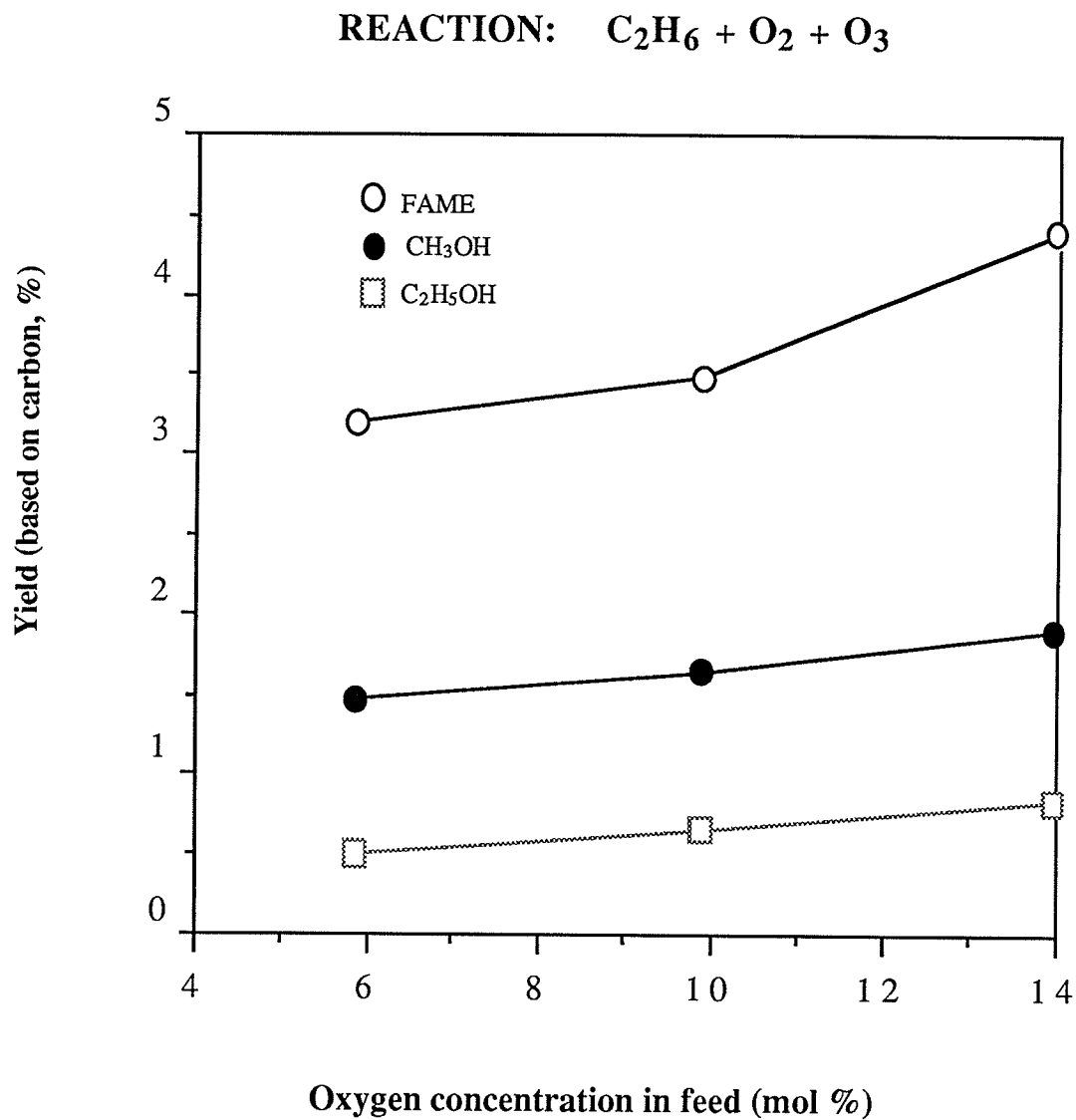


Figure 3.4-8. Variation of yield with  $O_2$  concentration in the feed

Residence time: 6.23-6.82 min.

S.V.: 6.29-6.89  $hr^{-1}$  (STP)

Reaction pressure: 1.45 atm

$O_3$  concentration in  $O_2$ : ca. 8 (wt)%

Reaction temperature: 281 °C

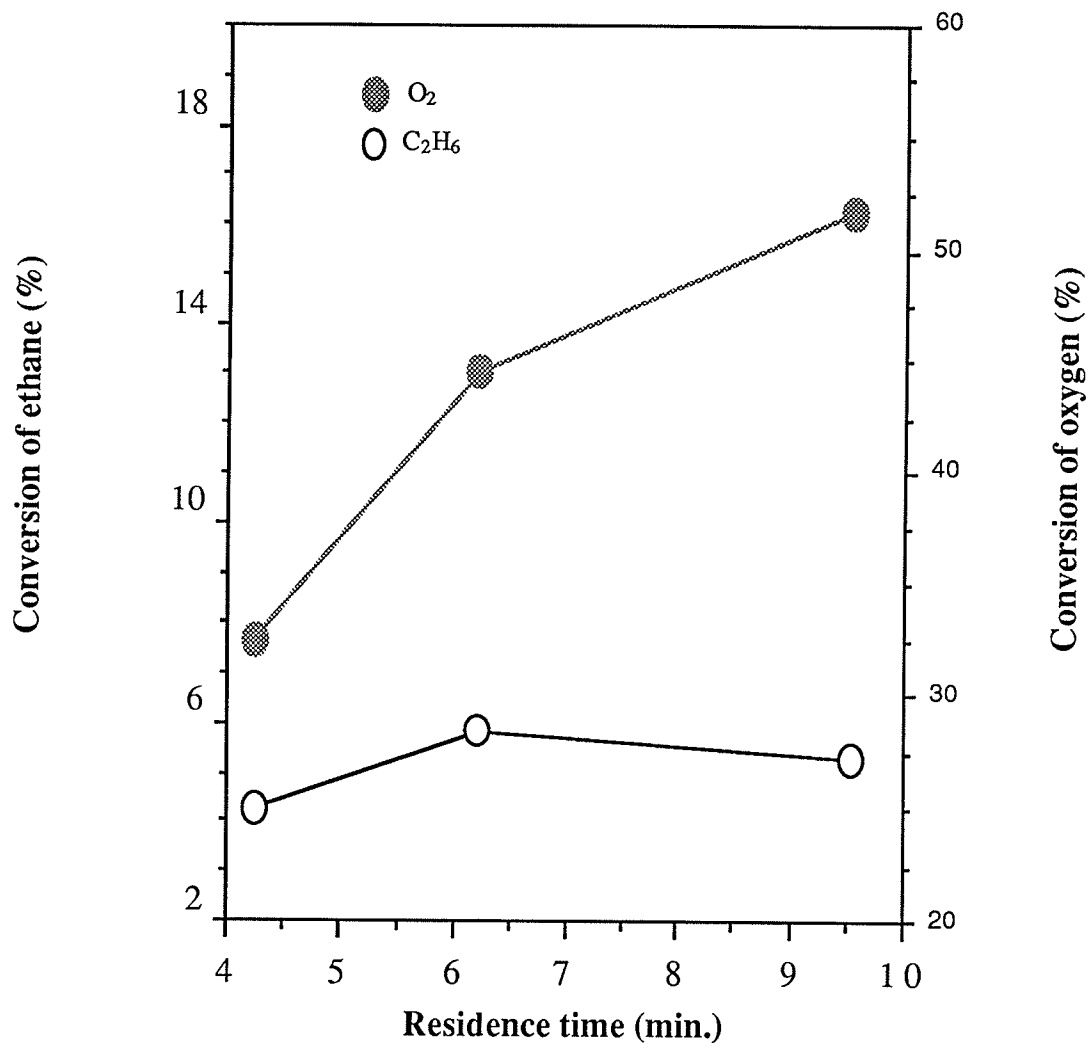
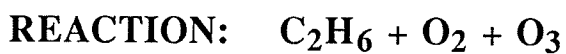


Figure 3.4-9. Variation of conversion with residence time

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 281 °C

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in the feed: 11.45-14.65 (mol)%

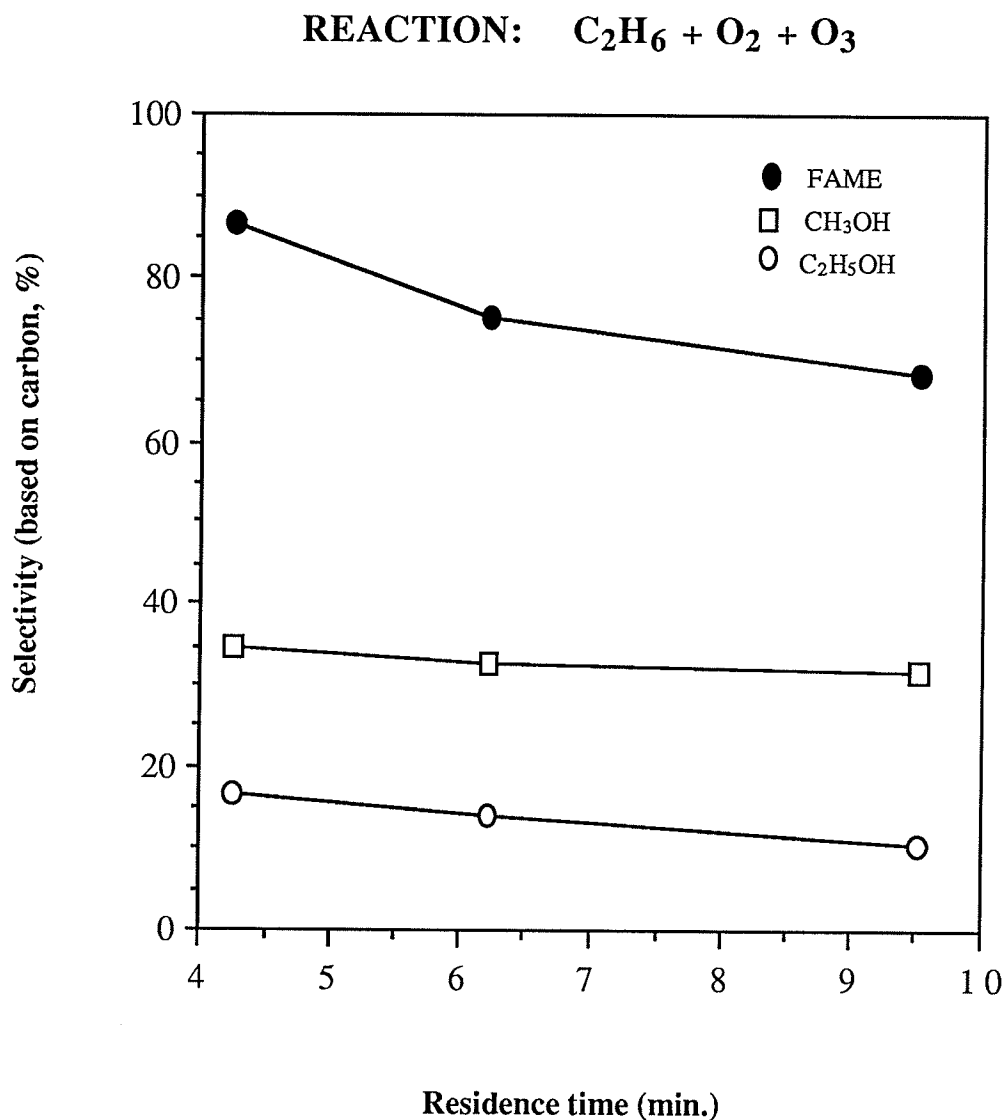


Figure 3.4-10a. Variation of selectivity with residence time

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 281 °C

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in the feed: 11.45-14.65 (mol)%



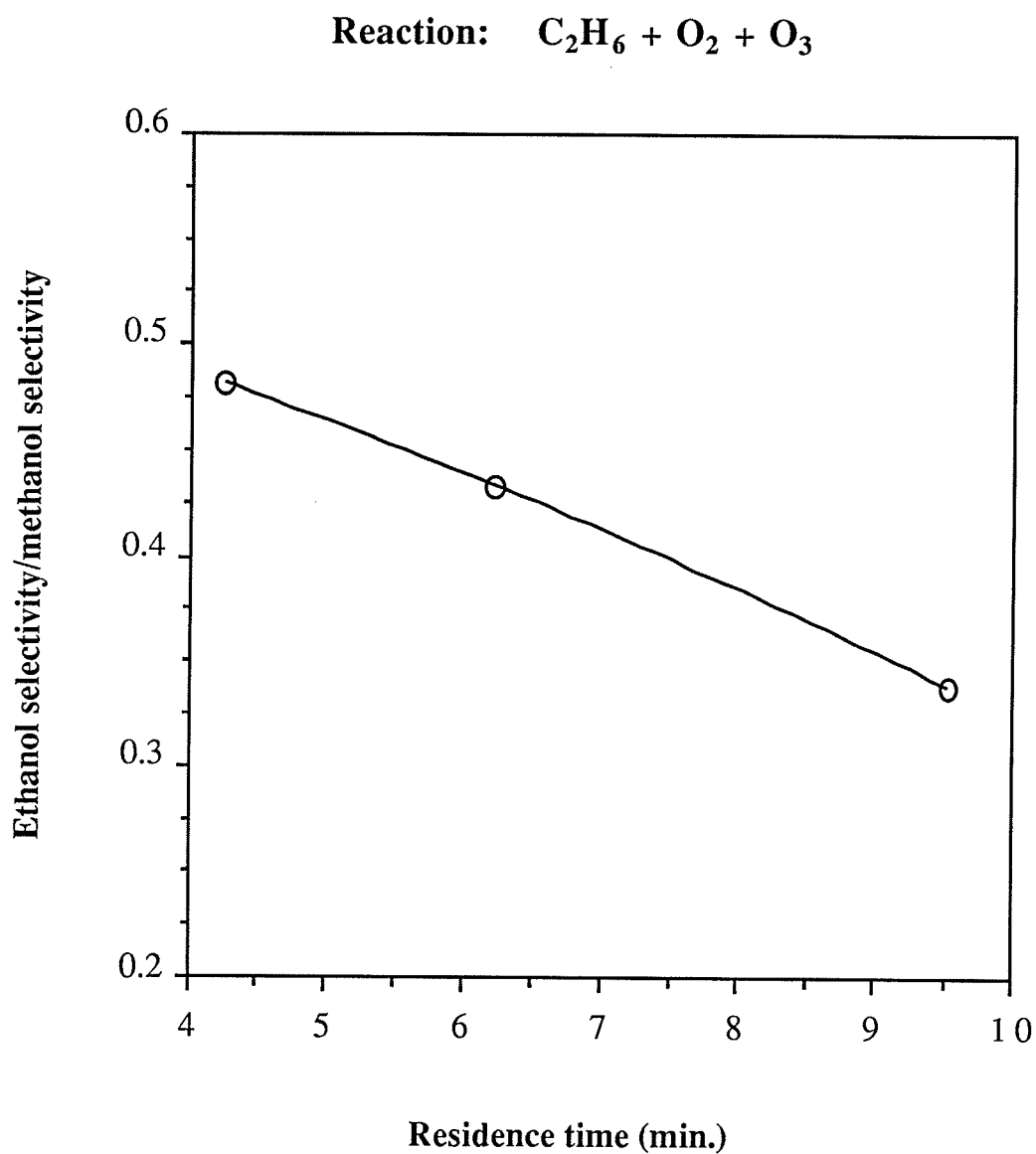


Figure 3.4-10b. Ethanol/methanol ratio as a function of residence time

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 281 °C

$\text{O}_3$  concentration in  $\text{O}_2$ : ca. 8 (wt)%

$\text{O}_2$  concentration in the feed: 11.45-14.65 (mol)%

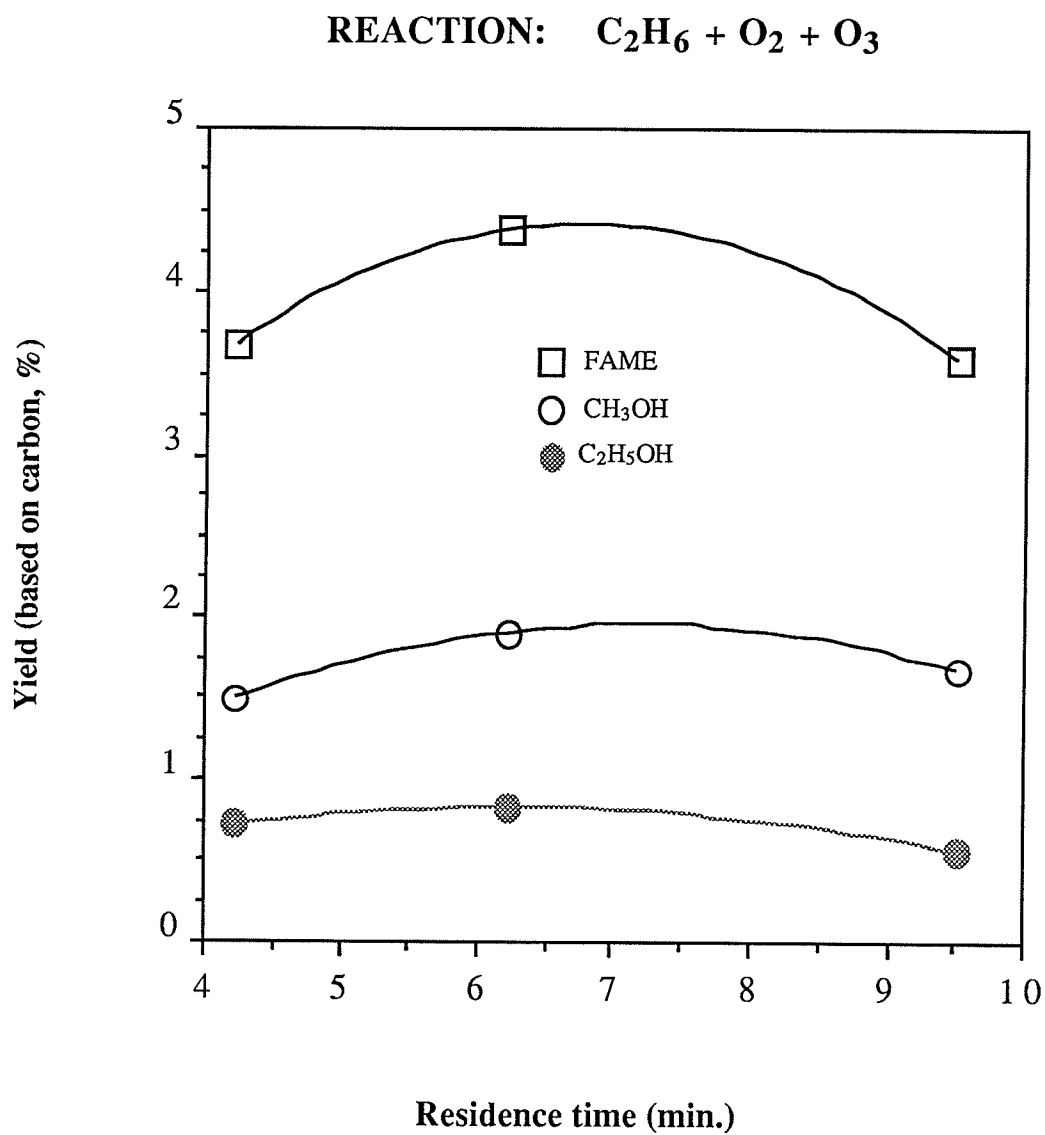


Figure 3.4-11. Variation of yield with residence time

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 281 °C

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in the feed: 11.45-14.65 (mol)%

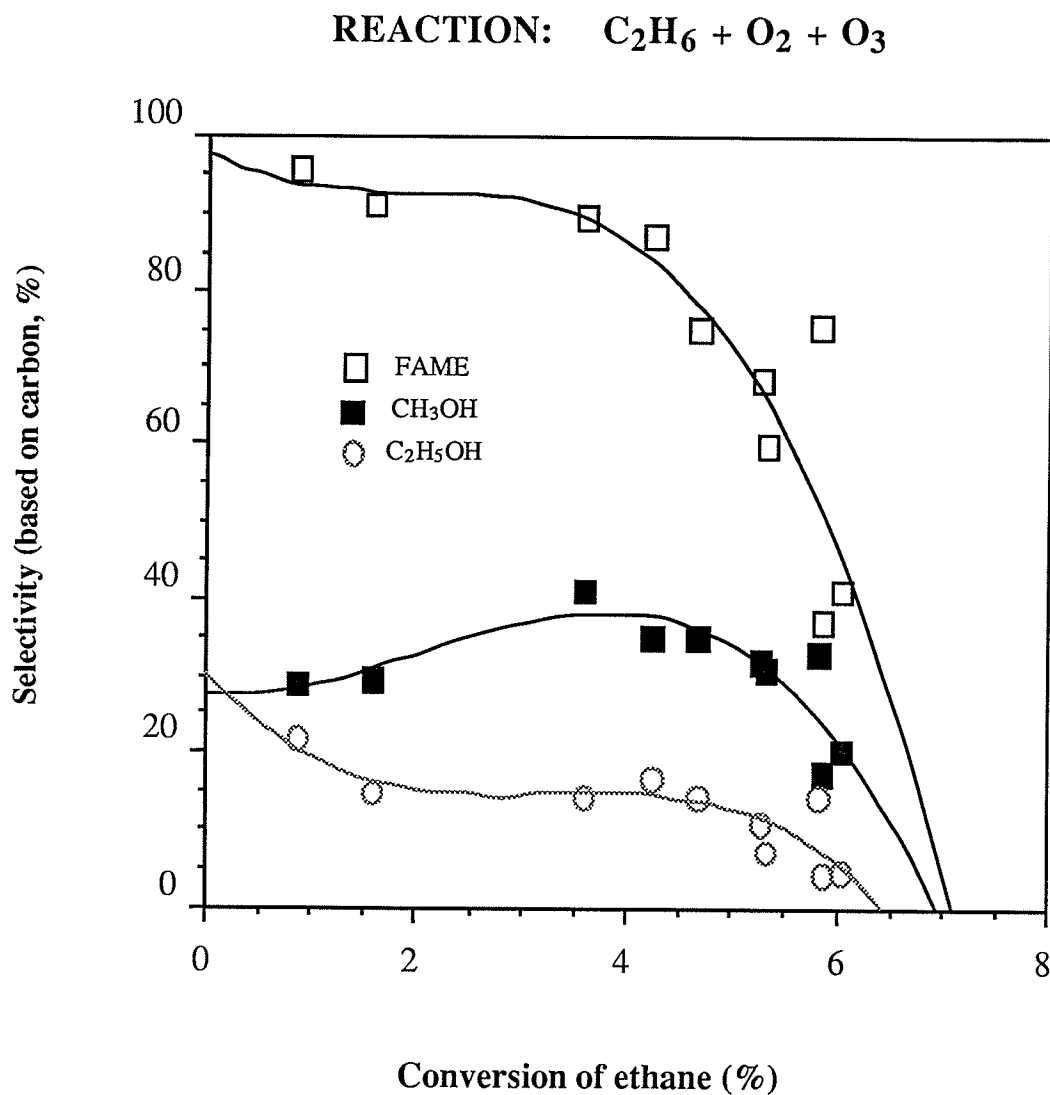


Figure 3.4-12 Variation of selectivity as a function of conversion

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 252-370 °C

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in the feed: 5.236-14.65 (mol)%

Residence time: 4.24-9.52 min.

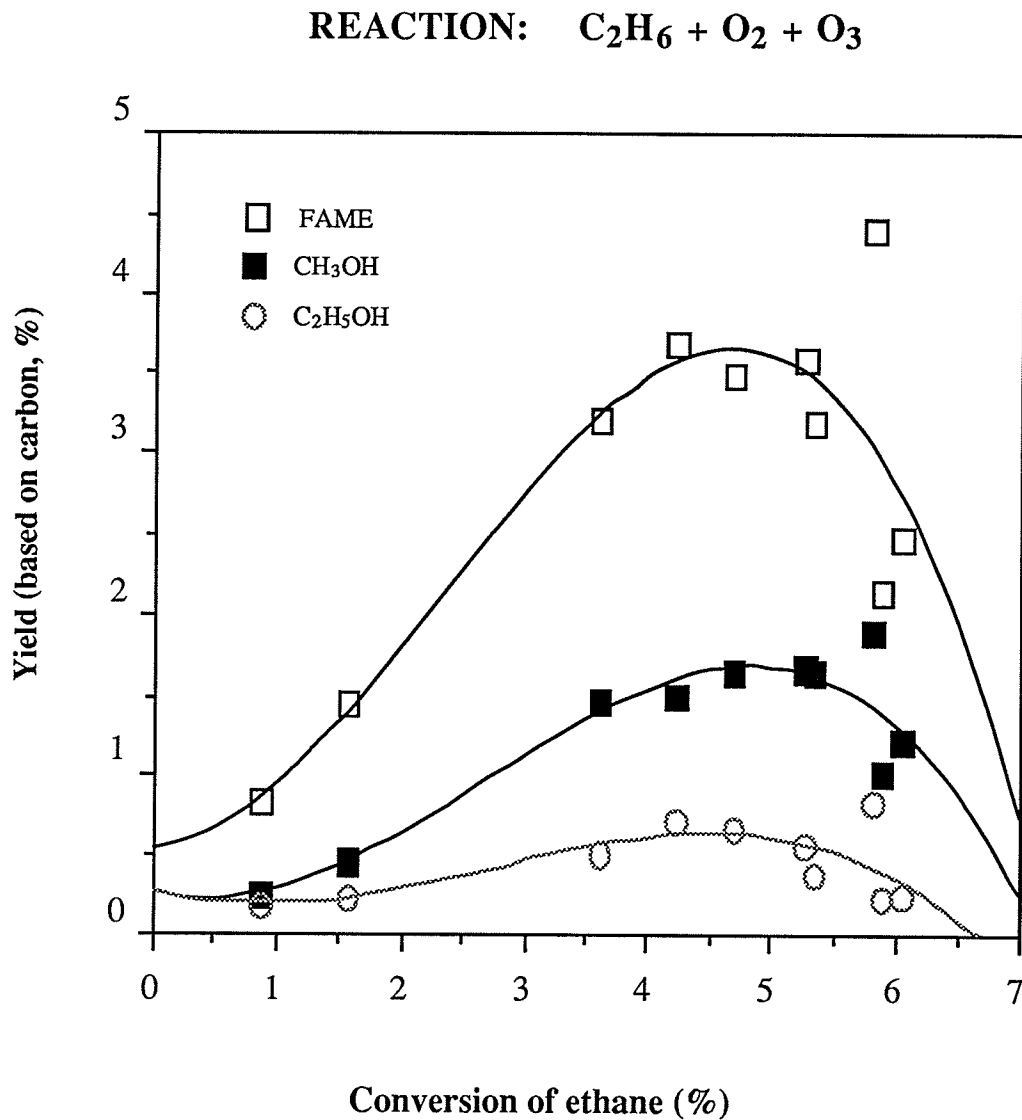


Figure 3.4-13. Variation of yield as a function of conversion

Reaction pressure: 1.35-1.55 atm

Reaction temperature: 252-370 °C

O<sub>3</sub> concentration in O<sub>2</sub>: ca. 8 (wt)%

O<sub>2</sub> concentration in the feed: 5.236-14.65 (mol)%

Residence time: 4.24-9.52 min.

## **CHAPTER IV**

## **CONCLUSION**

#### 4.1. Conclusions

From the present study, the following conclusions are drawn:

1. Ozone concentration generated by the spark method was very low ( $\sim 0.04$  wt % in  $O_2$  at 1 atm) but generated by the silent discharge method was much higher ( $\sim 8$  wt % in  $O_2$  at  $\sim 1.4$  atm).
2. Ozone can significantly sensitize both the methane-oxygen reaction and the ethane-oxygen reaction and enhance the formations of methanol and ethanol at near 1 atm pressure.
3. The ethane-oxygen reaction can be more easily initiated by ozone than the methane-oxygen reaction due to a lower hydrogen-carbon bond strength in ethane than in methane. At almost the same carbon conversion level ( $\sim 0.8\%$ ), the reaction temperature required for the ethane-oxygen reaction ( $252^\circ C$ ) was over  $120^\circ C$  lower than that required for the methane-oxygen reaction ( $375^\circ C$ ).
4. The reaction temperature, oxygen concentration in the feed, and residence time can significantly influence the conversions of the reactants and the selectivities of the products for both reactions. Among them, the reaction temperature is a most important influential factor.
5. The conversion of the reactants increased with increase in the reaction temperature for both reactions.

The selectivity and yield of methanol passed through their maximum values for methane reaction as the reaction temperature was raised, the further oxidation of methanol to carbon monoxide being responsible for the rapid decrease of the methanol selectivity at higher temperatures.

For the ethane reaction, as the reaction temperature was increased the selectivities of  $C_2H_5OH$ ,  $HCHO$ ,  $CH_3CHO$  and FAME and the E/M ratio decreased, the selectivity of  $CH_3OH$  passed through its maximum value, the CO selectivity was

inversely related to the FAME selectivity, and the yields of  $C_2H_5OH$ ,  $CH_3OH$  and FAME passed through their maximum values.

6. The conversion of  $O_2$  decreased but the conversions of methane and ethane increased as the  $O_2$  concentration was increased.

For the methane reaction, the selectivity of methanol decreased with increase in  $O_2$  concentration. The yield of methanol based on  $O_2$  decreased but the yield of methanol based on carbon did not change significantly as the  $O_2$  concentration in the feed was increased.

For the ethane reaction, as the  $O_2$  concentration was increased the  $CH_3OH$  and  $HCHO$  selectivities decreased, the  $C_2H_5OH$  selectivity remained almost constant, the FAME selectivity first decreased and then became almost independent of  $O_2$  concentration, the selectivities of FAME and CO were inversely related to each other, and the yield of  $C_2H_5OH$ ,  $CH_3OH$  and FAME increased.

7. The conversion of the reactants increased with increase in the residence time for the ethane reaction. However, for the methane reaction the conversions of the reactants obtained at higher residence time were higher than those obtained at shorter residence time.

The  $CH_3OH$  selectivity for the methane reaction and the  $C_2H_5OH$ ,  $CH_3OH$  and FAME selectivities as well as the E/M ratio for the ethane reaction increased with decrease in the residence time. The yields of  $C_2H_5OH$ ,  $CH_3OH$  and FAME for the ethane reaction passed through their maximum values.

8. The  $CH_3OH$  selectivity was a function of the methane conversion and it generally increased with the decrease of the methane conversion for the methane reaction. In order to obtain higher methanol selectivity ( $> 42\%$ ), the conversion of methane should be controlled at below  $1\%$ .

For the ethane reaction, the  $C_2H_5OH$ ,  $CH_3OH$  and FAME selectivities and yields as well as the E/M ratio were found to be a function of the conversion of

ethane. The  $C_2H_5OH$  and FAME selectivities and the E/M ratio increased with decrease in the conversion of ethane, whereas the  $CH_3OH$  selectivity passed through its maximum value as the conversion of ethane decreased. The yields of  $C_2H_5OH$ ,  $CH_3OH$  and FAME reached their highest values at almost the same ethane conversion level (~4.5 %).

9. For the methane reaction, the methanol selectivity was usually less than 50 %, but the combined methanol-formaldehyde-carbon monoxide selectivity was higher than 85 % (usually higher than 90 %). For the ethane reaction, although the ethanol and methanol selectivities were not high, the combined formaldehyde-acetaldehyde-methanol-ethanol (FAME) selectivities could be very high. If the ethane conversion is controlled at below 3.5 %, the FAME selectivity can reach over 90 %. The high FAME selectivity (over 85 %) can be obtained by operating at lower reaction temperature (252-280 °C) and lower  $O_2$  concentration (5-6 %) and shorter residence time (~6 min.)
10. The design and material of the reactor are very important to the reaction results. Pyrex glass is superior to steel material for construction of the reactor due to its relatively poor heat conductivity and its inertness which can reduce the decomposition of ozone in the temperature transition section at the entrance of the reactor.  
  
In order to maximize the effect of ozone sensitization, the reduction of the decomposition of ozone in the temperature transition section at the entrance of the reactor is an important factor which should be considered in designing a new reactor.
11. The conversion of methane and ethane increased with increase in concentration of ozone in  $O_2$ . The minimum ozone concentration in  $O_2$  at which the effect of sensitization could be observed was less than 1 wt %. There is a possibility that ozone sensitized methane-oxygen and ethane-oxygen reactions can be conducted at a higher pressure (e.g., 3-5 atm) if the concentration of ozone generated in  $O_2$  can reach more than 1 %.



12. Both the methane-oxygen reaction and the ethane-oxygen reaction proceeded by a free radical reaction mechanism. At lower reaction temperature the reaction was initiated by ozone and at higher reaction temperature the reactions proceeded by both the ozone initiation reaction and the ordinary homogeneous reaction.

#### **4.2. Suggestion for future work**

Increasing the methanol selectivity for the methane-oxygen reaction and the ethanol selectivity for the ethane-oxygen reaction is essential in the future work.

One of the important conclusions drawn from this research is that reduction of the residence time effects significant increases in the selectivities of methanol and ethanol. A higher reaction pressure (e.g., 3-5 atm) not only favors the formation of methanol and ethanol during reaction but also makes it possible for the ozone sensitized reactions to be conducted at shorter residence time (i.e., at higher flow rate) which should increase the methanol and ethanol selectivities significantly.

It seems worthwhile for future work to find a method by which the high ozone concentrations can be generated at higher pressure to initiate the reactions and permit a study of the methane-oxygen and the ethane-oxygen reaction at higher pressure in order to increase the methanol and ethanol selectivities.

## **APPENDIX A**

**THE OPERATION PARAMETERS FOR BOTH THE HP G.C.  
AND THE F-H G.P. AND THE OPERATION PROGRAM FOR  
THE PERKIN-ELMER SIGMA 10 DATA SYSTEM**

## 1. Operation parameters for HP G.C.

Flow rate of carrier gas (helium):	20.5 mL/min.
Temp. of thermal conductivity:	150 °C
Temp. of injection port:	150 °C
Column temp. program:	
initial	53 °C
hold	4 min.
rate of rise	8 °C/min
final	150 °C
hold	8 (or 16) min. for the methane reaction
	6 (or 32) min for the ethane reaction
Attenuator:	1
Voltage control:	6 V
Pressure before the column:	22.5 psig
Sampling valve temp.:	115 °C

## 2. Operation parameters for F-H G.P.

Flow rate of carrier gas (helium):	35.9 mL/min.
Temp. of the columns	22 °C.
Temp. of injection port:	21 °C
Cell current:	260 ma
Attenuate:	1

### 3. Operation program for Perkin-Elmer Sigma 10 Data System

#### ANALYZER CONTROL

INJ TEMP      25  
 DET ZONE      1.2      65      25  
 AUX TEMP      25  
 FLOW A,B      5      5  
 INIT OVEN TEMP, TIME      76      999

#### DATA PROC

STD WT, SMP WT      0.0000      1.0000      0  
 FACTOR, SCALE      1      0  
 TIMES      m\*      0.00      327.67      327.67      327.67      327.67  
 SENS-DET RANGE      50      n\*      0.00      2      0      0  
 UNK, AIR      1.000      0.00  
 TOL      0.0000      0.050      1.0  
 REF PK      0.000      0.00      0.00      0.00  
 STD NAME

#### EVENT CONTROL

ATTN-CHART-DELAY      0      5      0.01

m\* = 15 for analysis of the feed

24 (or 32) for analysis of the products of the methane reaction

32 (or 48) for analysis of the products of the ethane reaction

n\* = 2 (sometimes 1)

## **APPENDIX B**

### **THE DATA OF THE OZONE SENSITIZED METHANE-OXYGEN REACTION**

Experiment No. : 32

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 375 °C Reaction pressure : 1.3 atm.

Flow rate : 12.1 mL/min (STP) Residence time: 5.13 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.426	12.12
$\text{N}_2$	1.706	
$\text{CH}_4$	90.869	0.827

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	7.071				
$\text{N}_2$	1.735				
$\text{CO}$	0.277	37.18	14.18	0.307	1.72
$\text{CH}_4$	89.269				
$\text{CO}_2$	0.044	5.91	4.51	0.0489	0.547
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.019	5.12		0.0423	
$\text{H}_2\text{O}$	1.201		61.56		7.46
$\text{HCHO}$	0.160	21.45	8.18	0.177	0.992
$\text{CH}_3\text{OH}$	0.226	30.34	11.57	0.251	1.40

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.974	1.065	0.976	1.000

Experiment No. : 33

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 401 °C Reaction pressure : 1.3 atm.

Flow rate : 11.2 mL/min (STP) Residence time: 5.35 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.363	14.19
$\text{N}_2$	1.701	
$\text{CH}_4$	90.936	1.09

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	6.923				
$\text{N}_2$	1.738				
CO	0.499	50.98	21.78	0.554	3.09
$\text{CH}_4$	89.080				
$\text{CO}_2$	0.043	4.37	3.73	0.0474	0.530
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.013	2.63		0.0285	
$\text{H}_2\text{O}$	1.294		56.53		8.02
HCHO	0.125	12.77	5.46	0.139	0.774
$\text{CH}_3\text{OH}$	0.286	29.26	12.50	0.318	1.77

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.970	1.073	0.970	1.000

Experiment No. : 34

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 430 °C

Reaction pressure : 1.3 atm.

Flow rate : 11.0 mL/min (STP)

Residence time: 5.20 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.363	21.90
$\text{N}_2$	1.701	
$\text{CH}_4$	90.936	1.78

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	6.249				
$\text{N}_2$	1.732				
CO	0.959	59.83	27.35	1.06	5.99
$\text{CH}_4$	88.561				
$\text{CO}_2$	0.062	3.85	3.52	0.0684	0.771
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.014	1.75		0.0311	
$\text{H}_2\text{O}$	1.869		53.33		11.7
HCHO	0.133	8.29	3.79	0.147	0.830
$\text{CH}_3\text{OH}$	0.421	26.28	12.01	0.467	2.63

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.974	1.068	0.972	1.000



Experiment No. : 35

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 461 °C

Reaction pressure : 1.3 atm.

Flow rate : 10.4 mL/min (STP)

Residence time: 5.27 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.479	54.96
$\text{N}_2$	1.657	
$\text{CH}_4$	90.864	5.07

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	3.763				
$\text{N}_2$	1.733				
CO	3.422	74.95	37.27	3.80	20.5
$\text{CH}_4$	85.520				
$\text{CO}_2$	0.235	5.15	5.12	0.261	2.82
$\text{C}_2\text{H}_4$	0.005	0.22		0.011	
$\text{C}_2\text{H}_6$	0.032	1.41		0.0712	
$\text{H}_2\text{O}$	4.455		48.52		26.7
HCHO	0.130	2.84	1.41	0.144	0.777
$\text{CH}_3\text{OH}$	0.704	15.43	7.67	0.782	4.22

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.948	1.068	0.932	1.000

Experiment No. : 36

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 490 °C

Reaction pressure : 1.3 atm.

Flow rate : 9.13 mL/min (STP)

Residence time: 5.79 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.479	85.92
$\text{N}_2$	1.657	
$\text{CH}_4$	90.864	7.34

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	1.134				
$\text{N}_2$	1.740				
$\text{CO}$	5.159	77.97	37.29	5.72	32.0
$\text{CH}_4$	83.577				
$\text{CO}_2$	0.500	7.56	7.23	0.555	6.21
$\text{C}_2\text{H}_4$	0.060	1.81		0.133	
$\text{C}_2\text{H}_6$	0.154	4.66		0.342	
$\text{H}_2\text{O}$	7.147		51.65		44.38
$\text{HCHO}$	0.067	1.02	0.49	0.0747	0.418
$\text{CH}_3\text{OH}$	0.462	6.99	3.34	0.513	2.87

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.946	1.026	0.922	1.000

Experiment No. : 37

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 490 °C Reaction pressure : 1.4 atm.

Flow rate : 16.3 mL/min (STP) Residence time: 3.50 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.730	88.24
$\text{N}_2$	1.632	
$\text{CH}_4$	90.637	7.00

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	0.911				
$\text{N}_2$	1.725				
$\text{CO}$	4.823	76.36	35.29	5.35	31.1
$\text{CH}_4$	83.907				
$\text{CO}_2$	0.435	6.89	6.37	0.482	5.62
$\text{C}_2\text{H}_4$	0.056	1.78		0.125	
$\text{C}_2\text{H}_6$	0.168	5.31		0.372	
$\text{H}_2\text{O}$	7.365		53.89		47.5
$\text{HCHO}$	0.067	1.06	0.49	0.0740	0.43
$\text{CH}_3\text{OH}$	0.543	8.59	3.97	0.602	3.50

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.942	0.948	0.924	1.000

Experiment No. : 38

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 461 °C

Reaction pressure : 1.35 atm.

Flow rate : 17.0 mL/min (STP)

Residence time: 3.36 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	6.682	59.89
$\text{N}_2$	1.659	
$\text{CH}_4$	91.659	5.16

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	2.755				
$\text{N}_2$	1.745				
$\text{CO}$	3.650	76.77	44.37	3.96	26.6
$\text{CH}_4$	87.376				
$\text{CO}_2$	0.141	2.97	3.43	0.153	2.05
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.039	1.63		0.0840	
$\text{H}_2\text{O}$	3.408		41.43		24.8
$\text{HCHO}$	0.144	3.03	1.75	0.156	1.05
$\text{CH}_3\text{OH}$	0.742	15.61	9.02	0.806	5.40

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.956	0.977	0.933	1.000

Experiment No. : 39

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 430 °C

Reaction pressure : 1.4 atm.

Flow rate : 16.8 mL/min (STP)

Residence time: 3.69 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.182	36.84
$\text{N}_2$	1.686	
$\text{CH}_4$	91.133	3.23

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.901				
$\text{N}_2$	1.701				
CO	1.915	65.39	33.50	2.11	12.3
$\text{CH}_4$	87.737				
$\text{CO}_2$	0.070	2.39	2.45	0.0772	0.903
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.014	0.97		0.032	
$\text{H}_2\text{O}$	2.746		48.04		17.7
HCHO	0.158	5.39	2.76	0.174	1.02
$\text{CH}_3\text{OH}$	0.757	25.86	13.25	0.835	4.88

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.986	1.071	0.978	1.000

Experiment No. : 40

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 402 °C

Reaction pressure : 1.4 atm.

Flow rate : 17.1 mL/min (STP)

Residence time: 3.76 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	7.241	17.70
$\text{N}_2$	1.675	
$\text{CH}_4$	91.083	1.11

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	5.600				
$\text{N}_2$	1.716				
CO	0.374	36.93	15.54	0.410	2.75
$\text{CH}_4$	90.287				
$\text{CO}_2$	0.027	2.69	2.26	0.0298	0.400
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.015	3.05		0.0339	
$\text{H}_2\text{O}$	1.399		58.07		10.3
HCHO	0.139	13.74	5.78	0.153	1.02
$\text{CH}_3\text{OH}$	0.442	43.59	18.34	0.484	3.25

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.979	0.917	0.981	1.000

Experiment No. : 50

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 402 °C

Reaction pressure : 1.45 atm.

Flow rate : 17.5 mL/min (STP)

Residence time: 3.81 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	15.064	14.40
$\text{N}_2$	1.594	
$\text{CH}_4$	83.342	2.56

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	13.023				
$\text{N}_2$	1.489				
CO	1.353	63.33	30.87	1.62	4.45
$\text{CH}_4$	81.141				
$\text{CO}_2$	0.051	2.37	2.31	0.0608	0.333
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.016	1.52		0.0390	
$\text{H}_2\text{O}$	2.227		50.84		7.32
HCHO	0.225	10.55	5.14	0.271	0.740
$\text{CH}_3\text{OH}$	0.475	22.23	10.84	0.570	1.56

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
1.070	1.081	1.064	1.000

Experiment No. : 52

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 402 °C Reaction pressure : 1.5 atm.

Flow rate : 16.2 mL/min (STP) Residence time: 4.24 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	9.106	19.32
$\text{N}_2$	1.702	
$\text{CH}_4$	89.192	1.61

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	6.546				
$\text{N}_2$	1.631				
$\text{CO}$	0.799	54.98	25.47	0.886	4.921
$\text{CH}_4$	88.722				
$\text{CO}_2$	0.053	3.63	3.36	0.0584	0.649
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.018	2.49		0.0402	
$\text{H}_2\text{O}$	1.667		53.16		10.3
$\text{HCHO}$	0.172	11.82	5.47	0.190	1.06
$\text{CH}_3\text{OH}$	0.393	27.08	12.54	0.436	2.42

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
1.055	0.930	1.054	1.000



Experiment No. : 56

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 402 °C

Reaction pressure : 1.45 atm.

Flow rate : 17.2 mL/min (STP)

Residence time: 3.88 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	4.360	33.09
$\text{N}_2$	1.751	
$\text{CH}_4$	93.890	1.83

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	3.367				
$\text{N}_2$	1.717				
CO	0.912	53.44	27.39	0.978	9.06
$\text{CH}_4$	91.606				
$\text{CO}_2$	0.036	2.12	2.17	0.0387	0.718
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.016	1.86		0.0340	
$\text{H}_2\text{O}$	1.619		48.61		16.1
HCHO	0.146	8.58	4.40	0.157	1.46
$\text{CH}_3\text{OH}$	0.580	34.00	17.43	0.622	5.77

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
1.013	1.177	1.011	1.000

Experiment No. : 80

Reaction:  $\text{CH}_4 + \text{O}_2 + \text{O}_3$  (ca. 1.5 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 380 °C

Reaction pressure : 1.5 atm.

Flow rate : 19.6 mL/min (STP)

Residence time: 4.00 min.

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.751	16.50
$\text{N}_2$	1.891	
$\text{CH}_4$	92.357	0.773

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.632				
$\text{N}_2$	1.913				
CO	0.190	26.59	10.37	0.206	1.71
$\text{CH}_4$	91.628				
$\text{CO}_2$	0.024	3.37	2.62	0.0260	0.433
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	0.020	5.61		0.0433	
$\text{H}_2\text{O}$	1.133		61.88		10.2
HCHO	0.076	10.64	4.15	0.0822	0.684
$\text{CH}_3\text{OH}$	0.384	53.80	20.98	0.416	3.462

Ratio of Mass (out) to Mass (in) (based on nitrogen balance)			
Carbon	Oxygen	Hydrogen	Nitrogen
0.988	0.953	0.992	1.000

## **APPENDIX C**

### **THE DATA OF THE OZONE SENSITIZED ETHANE-OXYGEN REACTION**

Experiment No. : 59

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 352 °C      Reaction pressure : 1.45 atm.  
 Flow rate : 13.1 mL/min (STP)      Residence time: 5.49 min.  
 Space velocity: 6.92 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.698	98.32
$\text{CO}_2$	0.363	
$\text{C}_2\text{H}_6$	93.939	6.06

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	0.105				
$\text{CO}$	3.888	35.25	31.96	2.14	31.42
$\text{CH}_4$	1.551	14.06		0.852	
$\text{CO}_2$	0.523	1.54	2.78	0.0930	2.74
$\text{C}_2\text{H}_4$	0.390	7.07		0.428	
$\text{C}_2\text{H}_6$	85.529				
$\text{H}_2\text{O}$	3.976		32.68		32.13
$\text{HCHO}$	1.207	10.94	9.92	0.663	9.75
$\text{CH}_3\text{CHO}$	0.292	5.29	2.40	0.321	2.36
$\text{CH}_3\text{OH}$	2.228	20.20	18.31	1.22	18.0
$\text{C}_2\text{H}_5\text{OH}$	0.238	4.31	1.95	0.261	1.92
$\text{C}_4\text{H}_{10}$	0.074	1.34		0.081	
FAME*		40.74		2.465	
E/M*		0.213			
Alcohol*		24.51		1.481	
Aldehyde*		16.23		0.984	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.994	1.106	0.988

Experiment No. : 60

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 370 °C Reaction pressure : 1.45 atm.  
 Flow rate : 12.8 mL/min (STP) Residence time: 5.47 min.  
 Space velocity: 6.76 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.236	100
$\text{CO}_2$	0.374	
$\text{C}_2\text{H}_6$	94.390	5.87

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	0				
$\text{CO}$	3.801	35.35	33.28	2.08	33.3
$\text{CH}_4$	1.595	14.83		0.871	
$\text{CO}_2$	0.516	1.40	2.64	0.0823	2.64
$\text{C}_2\text{H}_4$	0.550	10.22		0.601	
$\text{C}_2\text{H}_6$	86.142				
$\text{H}_2\text{O}$	3.930		34.41		34.41
$\text{HCHO}$	0.985	9.16	8.62	0.538	8.62
$\text{CH}_3\text{CHO}$	0.349	6.49	3.05	0.381	3.05
$\text{CH}_3\text{OH}$	1.842	17.13	16.13	1.01	16.1
$\text{C}_2\text{H}_5\text{OH}$	0.212	3.95	1.86	0.232	1.86
$\text{C}_4\text{H}_{10}$	0.079	1.47		0.086	
FAME*		36.73		2.161	
E/M*		0.231			
Alcohol*		21.08		1.242	
Aldehyde*		15.65		0.919	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.994	1.110	0.988

Experiment No. : 65

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 281 °C Reaction pressure : 1.45 atm.  
 Flow rate : 11.9 mL/min (STP) Residence time: 6.82 min.  
 Space velocity: 6.29 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.842	58.15
$\text{CO}_2$	0.372	
$\text{C}_2\text{H}_6$	93.786	3.60

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	3.237				
$\text{CO}$	0.231	3.53	2.56	0.127	1.49
$\text{CH}_4$	0.001	0.011		0.0004	
$\text{CO}_2$	0.597	3.49	5.08	0.126	2.95
$\text{C}_2\text{H}_4$	0.121	3.71		0.134	
$\text{C}_2\text{H}_6$	87.505				
$\text{H}_2\text{O}$	3.400		37.79		22.0
$\text{HCHO}$	1.305	19.97	14.51	0.719	8.44
$\text{CH}_3\text{CHO}$	0.459	14.06	5.11	0.506	2.97
$\text{CH}_3\text{OH}$	2.680	41.02	29.79	1.48	17.3
$\text{C}_2\text{H}_5\text{OH}$	0.464	14.21	5.16	0.511	3.00
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		89.26		3.216	
E/M*		0.346			
Alcohol*		55.23		1.991	
Aldehyde*		34.03		1.225	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.976	1.315	0.986

Experiment No. : 66

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 252 °C Reaction pressure : 1.35 atm.  
 Flow rate : 13.2 mL/min (STP) Residence time: 6.06 min.  
 Space velocity: 6.95  $\text{hr}^{-1}$  (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	6.587	18.28
$\text{CO}_2$	0.365	
$\text{C}_2\text{H}_6$	93.048	0.869

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.818				
$\text{CO}$	0	0	0	0	0
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.434	4.33	6.54	0.0377	1.19
$\text{C}_2\text{H}_4$	0	0		0	
$\text{C}_2\text{H}_6$	92.732				
$\text{H}_2\text{O}$	0.852		39.52		7.22
$\text{HCHO}$	0.305	18.72	14.13	0.163	2.58
$\text{CH}_3\text{CHO}$	0.216	26.57	10.02	0.231	1.83
$\text{CH}_3\text{OH}$	0.465	28.61	21.59	0.249	3.95
$\text{C}_2\text{H}_5\text{OH}$	0.177	21.76	8.21	0.189	1.50
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		95.66		0.832	
E/M*		0.761			
Alcohol*		50.37		0.438	
Aldehyde*		45.29		0.394	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
1.007	0.902	1.010

Experiment No. : 67

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 281 °C Reaction pressure : 1.45 atm.  
 Flow rate : 12.3 mL/min (STP) Residence time: 6.58 min.  
 Space velocity: 6.51 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	9.889	53.63
$\text{CO}_2$	0.342	
$\text{C}_2\text{H}_6$	89.769	4.68

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.958				
$\text{CO}$	1.477	17.99	12.88	0.843	6.91
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.735	4.83	6.91	0.226	3.71
$\text{C}_2\text{H}_4$	0.107	2.60		0.122	
$\text{C}_2\text{H}_6$	83.527				
$\text{H}_2\text{O}$	4.051		35.33		18.9
$\text{HCHO}$	1.299	15.82	11.33	0.741	6.07
$\text{CH}_3\text{CHO}$	0.406	9.90	3.54	0.464	1.90
$\text{CH}_3\text{OH}$	2.869	34.95	25.02	1.64	13.42
$\text{C}_2\text{H}_5\text{OH}$	0.571	13.91	4.98	0.652	2.67
$\text{C}_4\text{H}_{10}$					
FAME*		74.58		3.497	
E/M*		0.398			
Alcohol*		48.86		2.292	
Aldehyde*		25.72		1.205	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.988	1.091	0.994



Experiment No. : 68

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 281 °C Reaction pressure : 1.45 atm.  
 Flow rate : 13.0 mL/min (STP) Residence time: 6.23 min.  
 Space velocity: 6.89 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	13.962	44.46
$\text{CO}_2$	0.346	
$\text{C}_2\text{H}_6$	85.692	5.82

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	8.676				
$\text{CO}$	1.599	16.69	11.51	0.971	5.12
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.899	5.82	8.03	0.339	3.57
$\text{C}_2\text{H}_4$	0.103	2.14		0.125	
$\text{C}_2\text{H}_6$	77.544				
$\text{H}_2\text{O}$	5.275		37.97		16.9
$\text{HCHO}$	1.465	15.29	10.54	0.889	4.69
$\text{CH}_3\text{CHO}$	0.639	13.35	4.60	0.777	2.05
$\text{CH}_3\text{OH}$	3.123	32.60	22.48	1.90	10.0
$\text{C}_2\text{H}_5\text{OH}$	0.676	14.11	4.87	0.821	2.16
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		75.35		4.387	
E/M*		0.433			
Alcohol*		46.71		2.721	
Aldehyde*		28.64		1.666	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.975	1.132	0.983

Experiment No. : 69

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 281 °C Reaction pressure : 1.55 atm.  
 Flow rate : 20.5 mL/min (STP) Residence time: 4.24 min.  
 Space velocity: 10.8 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	14.645	32.57
$\text{CO}_2$	0.338	
$\text{C}_2\text{H}_6$	85.018	4.24

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	10.732				
$\text{CO}$	0.326	4.66	3.14	0.198	1.02
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.760	6.09	8.21	0.258	2.67
$\text{C}_2\text{H}_4$	0.085	2.43		0.103	
$\text{C}_2\text{H}_6$	78.908				
$\text{H}_2\text{O}$	4.256		41.05		13.4
$\text{HCHO}$	1.356	19.40	13.08	0.823	4.26
$\text{CH}_3\text{CHO}$	0.544	15.56	5.24	0.660	1.71
$\text{CH}_3\text{OH}$	2.447	35.02	23.60	1.48	7.69
$\text{C}_2\text{H}_5\text{OH}$	0.588	16.84	5.67	0.714	1.85
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		86.82		3.677	
E/M*		0.481			
Alcohol*		51.86		2.194	
Aldehyde*		34.96		1.483	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.980	1.096	0.992

Experiment No. : 70

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 281 °C Reaction pressure : 1.35 atm.  
 Flow rate : 7.94 mL/min (STP) Residence time: 9.52 min.  
 Space velocity: 4.19 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	11.453	51.60
$\text{CO}_2$	0.348	
$\text{C}_2\text{H}_6$	88.199	5.26

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	5.778				
$\text{CO}$	2.257	24.87	18.32	1.31	9.45
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.693	3.86	5.68	0.203	2.93
$\text{C}_2\text{H}_4$	0.135	2.98		0.156	
$\text{C}_2\text{H}_6$	81.776				
$\text{H}_2\text{O}$	4.220		34.26		17.7
$\text{HCHO}$	1.205	13.28	9.78	0.698	5.05
$\text{CH}_3\text{CHO}$	0.569	12.54	4.62	0.659	2.38
$\text{CH}_3\text{OH}$	2.883	31.77	23.40	1.67	12.1
$\text{C}_2\text{H}_5\text{OH}$	0.486	10.71	3.94	0.563	2.03
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		68.30		3.590	
E/M*		0.337			
Alcohol*		42.48		2.233	
Aldehyde*		25.82		1.357	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.992	1.055	0.994

Experiment No. : 71

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III  
 Reaction temperature : 300 °C Reaction pressure : 1.45 atm.  
 Flow rate : 12.8 mL/min (STP) Residence time: 6.14 min.  
 Space velocity: 6.75 hr<sup>-1</sup> (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.713	97.74
$\text{CO}_2$	0.377	
$\text{C}_2\text{H}_6$	93.910	5.33

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	0.136				
$\text{CO}$	2.871	29.20	24.54	1.56	24.0
$\text{CH}_4$	0.500	5.08		0.271	
$\text{CO}_2$	0.543	1.75	2.95	0.0935	2.88
$\text{C}_2\text{H}_4$	0.195	3.97		0.212	
$\text{C}_2\text{H}_6$	87.256				
$\text{H}_2\text{O}$	3.385		28.94		28.3
$\text{HCHO}$	1.286	13.08	11.00	0.698	10.7
$\text{CH}_3\text{CHO}$	0.419	8.52	3.58	0.454	3.50
$\text{CH}_3\text{OH}$	3.042	30.94	26.01	1.65	25.4
$\text{C}_2\text{H}_5\text{OH}$	0.350	7.13	3.00	0.380	2.93
$\text{C}_4\text{H}_{10}$	0.017	0.34		0.018	
FAME*		59.67		3.182	
E/M*		0.230			
Alcohol*		38.07		2.030	
Aldehyde*		21.60		1.152	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.996	1.059	0.994

Experiment No. : 72

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 8 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 267 °C

Reaction pressure : 1.4 atm.

Flow rate : 12.9 mL/min (STP)

Residence time: 6.24 min.

Space velocity: 6.81  $\text{hr}^{-1}$  (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	5.520	32.65
$\text{CO}_2$	0.365	
$\text{C}_2\text{H}_6$	94.115	1.58

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.142				
CO	0.149	5.04	3.70	0.0799	1.21
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.438	2.55	3.74	0.0404	1.22
$\text{C}_2\text{H}_4$	0.024	1.66		0.0263	
$\text{C}_2\text{H}_6$	91.530				
$\text{H}_2\text{O}$	1.575		39.22		12.80
HCHO	0.740	25.11	18.43	0.398	6.02
$\text{CH}_3\text{CHO}$	0.316	21.45	7.87	0.340	2.57
$\text{CH}_3\text{OH}$	0.869	29.49	21.64	0.467	7.07
$\text{C}_2\text{H}_5\text{OH}$	0.217	14.70	5.39	0.233	1.76
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		90.75		1.438	
E/M*		0.499			
Alcohol*		44.19		0.700	
Aldehyde*		46.56		0.738	

\* FAME = HCHO +  $\text{CH}_3\text{OH}$  +  $\text{CH}_3\text{CHO}$  +  $\text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH}$  +  $\text{C}_2\text{H}_5\text{OH}$ \* Aldehyde = HCHO +  $\text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.992	1.111	0.995

Experiment No. : 74

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 2.4 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 280 °C

Reaction pressure : 1.45 atm.

Flow rate : 12.4 mL/min (STP)

Residence time: 6.56 min.

Space velocity: 6.55  $\text{hr}^{-1}$  (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	9.277	51.14
$\text{CO}_2$	0.408	
$\text{C}_2\text{H}_6$	90.315	4.18

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	4.716				
$\text{CO}$	1.492	20.10	15.11	0.839	7.73
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.628	3.02	4.54	0.126	2.32
$\text{C}_2\text{H}_4$	0.086	2.32		0.0968	
$\text{C}_2\text{H}_6$	85.147				
$\text{H}_2\text{O}$	3.378		34.22		17.5
$\text{HCHO}$	1.263	17.02	12.79	0.711	6.54
$\text{CH}_3\text{CHO}$	0.532	14.33	5.39	0.598	2.75
$\text{CH}_3\text{OH}$	2.310	31.12	23.40	1.30	12.0
$\text{C}_2\text{H}_5\text{OH}$	0.449	12.10	4.55	0.505	2.33
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		74.57		3.114	
E/M*		0.389			
Alcohol*		43.22		1.805	
Aldehyde*		31.35		1.309	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.994	1.049	0.997

Experiment No. : 76

Reaction:  $\text{C}_2\text{H}_6 + \text{O}_2 + \text{O}_3$  (ca. 1 wt % in  $\text{O}_2$ ), carried out in Reactor III

Reaction temperature : 280 °C

Reaction pressure : 1.45 atm.

Flow rate : 12.7 mL/min (STP)

Residence time: 6.41 min.

Space velocity: 6.70  $\text{hr}^{-1}$  (STP)

Compound	Feed composition (mol %)	Conversion (%)
$\text{O}_2$	8.811	27.49
$\text{CO}_2$	0.366	
$\text{C}_2\text{H}_6$	90.823	2.03

Compound	Output composition (mol %)	Selectivity (%), based on		Yield (%), based on	
		Carbon	Oxygen	Carbon	Oxygen
$\text{O}_2$	6.989				
$\text{CO}$	0.452	12.45	8.52	0.253	2.34
$\text{CH}_4$	0	0		0	
$\text{CO}_2$	0.447	2.30	3.15	0.0468	0.866
$\text{C}_2\text{H}_4$	0.070	3.84		0.0780	
$\text{C}_2\text{H}_6$	87.361				
$\text{H}_2\text{O}$	2.233		42.13		11.58
$\text{HCHO}$	0.844	23.25	15.92	0.473	4.38
$\text{CH}_3\text{CHO}$	0.322	17.77	6.08	0.361	1.67
$\text{CH}_3\text{OH}$	1.099	30.30	20.74	0.616	5.70
$\text{C}_2\text{H}_5\text{OH}$	0.183	10.09	3.45	0.205	0.949
$\text{C}_4\text{H}_{10}$	0	0		0	
FAME*		81.41		1.655	
E/M*		0.333			
Alcohol*		40.39		0.821	
Aldehyde*		41.02		0.834	

\* FAME =  $\text{HCHO} + \text{CH}_3\text{OH} + \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH}$ \* E/M =  $\text{C}_2\text{H}_5\text{OH}/\text{CH}_3\text{OH}$ \* Alcohol =  $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$ \* Aldehyde =  $\text{HCHO} + \text{CH}_3\text{CHO}$ 

Ratio of Mass (out) to Mass (in) (based on total mass balance)		
Carbon	Oxygen	Hydrogen
0.989	1.098	0.993

## **APPENDIX D**

### **THE LITERATURE VALUES OF THE RELATIVE RESPONSE FACTORS**



The literature values of the Relative Response Factors (RRF)

Compound	RRF
N <sub>2</sub>	1.46 <sup>a</sup>
O <sub>2</sub>	1.14 <sup>b</sup>
CO	1.51 <sup>a</sup>
CO <sub>2</sub>	2.08 <sup>a</sup>
CH <sub>4</sub>	1.00 <sup>a</sup>
C <sub>2</sub> H <sub>4</sub>	1.48 <sup>a</sup>
C <sub>2</sub> H <sub>6</sub>	1.50 <sup>a</sup>
H <sub>2</sub> O	0.736 <sup>b</sup>
HCHO	1.23 <sup>b</sup>
CH <sub>3</sub> OH	2.01 <sup>a</sup>
CH <sub>3</sub> CHO	2.13 <sup>c</sup>
C <sub>2</sub> H <sub>5</sub> OH	2.08 <sup>a</sup>
C <sub>4</sub> H <sub>10</sub>	1.96 <sup>a</sup>

a: calculated from Reference 51 (TCD at 100 °C)

b: taken from Reference 40

c: calculated from Reference 52

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