

CATALYTIC THERMOCONVERSION OF CELLULOSE TO FUELS IN AQUEOUS MEDIUM

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ABSTRACT

Catalytic thermochemical liquefaction in aqueous medium was studied for conversion of cellulose to liquid fuels. There are 8 reactions were done by two different co-catalysts, (alkaline & acidic) with 5% Pt/Al₂O₃ in presence of 35 bar CO and H₂ as a reducing gas, at 300 °C. The duration of reaction time was 2 hours. During the reactions, catalysts and reaction time affected the process most dramatically. While the initial liquefaction (depolymerisation) of the cellulose is thermally controlled (pyrolysis), the subsequent conversion of the "Proto-oil" to liquid oils (deoxygenation) is mainly catalytically influenced. Some of the catalysts exhibited effective deoxygenation which resulted in the conversion of "Proto-oil" to a low oxygen content product. In run 7, conversion, oil production, H/C atomic ratio, calorific value is higher than others.

INTRODUCTION:

The conversion of cellulose to liquid fuels has been the subject of intensive studies during the last years¹⁻³.

The key problem in the liquefaction of biomass is the poor control of desired reactions. In pyrolytic liquefaction processes, the reactions are non selective, involving homolytic cleavage and free-radical reactions. In direct liquefaction, which uses CO, H₂, and water as reagent and catalysts, there is a complex sequence of reactions which probably starts out with the thermal breakdown of lignocellulosic materials and continues through the rearrangement, the reduction, the dehydration, the decarboxylation and other reactions to give a host of reactive compounds. These compounds can go further during the severe conditions of liquefaction process to lead to the polymerized, polymerisable and acidic compounds responsible of the poor yield and quality of the cellulose derived oil.

The crystalline regions in the cellulosic material make heterogeneous reactions occur slowly, as the close packing of the cellulose chains does not permit ease penetration by reagent molecules⁴. The use of homogeneous catalysts in these cases eliminates additional problems arising from the lack of effective contact between two solid phases, namely a heterogeneous catalyst and the biomass feedstock. Lindemuth⁵ believed that HCOO⁻ ion is the active species in a complex sequence of reactions that leads to oil formation.

The objective is to develop a consistent, quantified description of the liquefaction of cellulose, to examine the effect of co-catalysts with 5% Pt/Al₂O₃ in CO and H₂ atmosphere, quality of produced oils, and different types of water soluble components.

EXPERIMENTAL:

One liter capacity stainless steel autoclave (with rocker system) was used for each reaction with 1g different catalysts, 400g distilled water, 35 bar hydrogen gas and 300 °C temperature. All reactions were done for 2 hours. After cooling the autoclave, gasses were vented to the gas measurement system and collected samples for analysis in IR, GC. Then opened the autoclave for decant the aqueous layer and the rest of solid part was dissolved in acetone and refluxed for 3 hours, then filtered with vacuum pressure. After filtration, the solid part was char and catalyst; and the filtrate was rotaevaporated to separate acetone and oil. The remaining oil was separated by different solvents, such as Heptane and Toluene. The separated parts are called lights, waxes, asphaltenes and resins.

The aqueous phase contains a significant amount of reactive compounds, resulting from the breakdown of the cellulose. To understand of the nature of this complex, water soluble fraction, group separation was necessary before any identification was attempted. This was possible by solvent extraction. Prior to group separation, resinous substances from the water soluble were first precipitated with di-ethyl ether. The resulting ethereal soluble fraction was subsequently fractionated into four basic groups, namely; a) Carboxylic acids, (separated by 10% aqueous Na₂CO₃), b) Carbonyl compounds, (separated by 5% NaHSO₄), c) Phenolic compounds, (separated by 10% NaOH) and d) Solubilized/ Neutral hydrocarbons.

The four groups were identified by IR Spectroscopy.

IR - Perkin - Elmer IR Spectrophotometer (model 157) with range of 600 - 4000 cm⁻¹ was used.

Gas Chromatography - Pye Unicam G. C. (Series 204) fitted with dual detector system and coupled to a data processing computer (Hewlett - Packard - Data Dynamics 390) was used.

Catalysts - Johnson - Matthey Co. Cellulose - Powered pure cellulose (Solka-floc Brown Co., N. Y.).

Suspension medium water - Distilled water. **Reducing gases** - Electrolytic hydrogen and Carbon-monoxide, BOC commercial grade-99.5%.

RESULTS AND DISCUSSIONS:

Table 1, lists the different reaction inputs, operating parameters and product distribution for runs 1-8. K₂CO₃ and SnCl₂ were used as a Co-catalysts with 5% Pt/Al₂O₃ for conversion of cellulose (Solka-floc) at 300°C and 35 bar of CO and H₂ as a reducing gas with 400 g water. In case of SnCl₂ in H₂ atmosphere, the amount of H₂O formation is larger than with K₂CO₃ and CO atmospheres due to the dehydration and catalytic deoxygenation of cellulose. Here Sn⁺² plays an important role which enters into the complex scheme of reaction to reduce cellulose fragments and liberate O₂, which reacts with H₂ from atmosphere or (from solvent H₂O) to form H₂O. This homogeneous hydrogenation of acidic catalyst contributes to dehydration of cellulose and leads to produce unsaturated substances that polymerise easily to form char. This effect, is directly proportional to the acidity of the medium. On the other hand, K₂CO₃ with CO atmosphere, CO reacts with H₂O (from solvent) to form CO₂ and H₂ (water gas shift reaction) instead of produce H₂O. Hence, SnCl₂ with H₂ produces large amounts of H₂O.

Moreover, SnCl_2 with H_2 atmosphere, maximum amount of water-soluble compounds were formed due to the strong hydrolytic action of the acidic catalyst. But in case of K_2CO_3 in presence of CO atmosphere, is reverse due to the neutralization of the organic acid compounds, higher conversion to gasification and decarboxylation (loss of CO_2) of water soluble fractions and cellulose fractions. CO probably has an additional role which inhibits the polymerisation of unsaturated compounds to form char.

The product gas recovery, shown that the gas formation is greater in presence of K_2CO_3 with CO reactions, which is probably due to CO took part in the water-gas shift reaction as well as $\text{K}_2\text{CO}_3 + \text{CO} + \text{H}_2\text{O}$ can form intermediate compound, possibly a potassium formate, which produces hydrogen, probably as hydried (H) ion. This ion reacts with the substrate (cellulose fragments), to remove oxygen as CO_2 and leads to the formation of oil also.



Net reaction: $\text{H}_2\text{O} + \text{CO} < \longrightarrow \text{H}_2 + \text{CO}_2$

Table 2 shows the elemental analysis of the feeds, char and oil of run (from 1-8).

The H/C atomic ratio is higher (1.26) with 5% $\text{Pt}/\text{Al}_2\text{O}_3 + \text{K}_2\text{CO}_3 + \text{CO}$ atmosphere in run 7, which may be due to elimination of higher amount of oxygen as a CO_2 by water-gas shift reaction. That means one carbon atom can eliminates two oxygen atoms as CO_2 from the reaction mixture. But in case of SnCl_2 with H_2 , reduction occurs by the elimination of only one oxygen atom (as H_2O) with two hydrogen atoms. The total elimination of oxygen (reduction) is double in case of $\text{K}_2\text{CO}_3 + \text{CO}$ than $\text{SnCl}_2 + \text{H}_2$. Moreover, the produced hydried (H) ion, from potassium formate is more active reducing agent than normal hydrogen atmosphere. So, it can easily more reduced the cellulose fragments for production of high amount and high quality of oils. Hence, the H/C atomic ratio and calorific value of the run 7 is greater than run 6 and others. is also high.

After solvent analysis, high amount of lights was formed than asphaltenes (in run 7) which was probably due to higher conversion of asphaltenes, resins and water-soluble fractions in presence of CO atmosphere into lights as well as gases (as CO_2 , CO and hydrocarbon gases) Which is shown in table 3.

From table 4, it is seen that when conversion increases, the production of water soluble fraction decreases and production of gases and oils increases. Moreover, ether soluble fractions from water soluble parts were also decreases on the same way which may due to the conversion of water soluble fractions into gases and oils. The ether soluble fractions were further separated by different solutions into different functional groups as carboxylic acid, carbonyl, phenolic and neutral hydrocarbons and identified by IR spectrum (shown in figure 1A to 2A).

From table 5, the G.C. analysis shown that K_2CO_3 in presence of CO atmosphere, CO_2 , CO gases are formed greater than the run with SnCl_2 in presence of H_2 which may probably due to water-gas shift reaction. The low concentration of hydrogen gases produced indicated that the hydrogen from the water-gas shift reaction is very reactive and reacts instantly with the cellulose fragments. The gases were identified by IR spectrum and GC chromatograms of run 5 to 8 and shown in figure 3A to 6A.

CONCLUSION:

- 1) In terms of conversion of cellulose, oil yield, quality of oil, calorific value of oil are higher in run 7, ($\text{K}_2\text{CO}_3 + 5\% \text{Pt}/\text{Al}_2\text{O}_3$ with CO atmosphere) in comparison with others.
- 2) The aqueous phase contains a significant amount of reactive compounds, resulting from the breakdown of the cellulose. The acidity of the aqueous phase is high ($\text{pH} \approx 3$) due to the presence of carboxylic acids. After reaction, when it was decanted from the autoclave, it looks as white after some while it becomes brown in color due to oxidation. After analysis of the water soluble fractions, it is seen that it contains carboxylic acids, carbonyl compounds, phenolic compounds and neutral hydrocarbon compounds, Table 5.
- 3) Using K_2CO_3 as a co-catalyst with 5% $\text{Pt}/\text{Al}_2\text{O}_3$ in presence of CO atmosphere, increased the yield of gaseous products at the expense of char and water soluble fraction. The improvement in the conversion has an reflection on the quantity and quality of the desired product.
- 4) The use of K_2CO_3 with 5% $\text{Pt}/\text{Al}_2\text{O}_3$ in presence of CO atmospheres had an enhanced effect on the catalytic conversion of cellulose.
- 5) Economically, 5% $\text{Pt}/\text{Al}_2\text{O}_3 + \text{SnCl}_2$ in presence of H_2 atmosphere is a viable catalyst for liquefaction of cellulose, because CO is more expensive than H_2 .

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Table 1. Reaction inputs, parameters and product distribution

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------------------------------|--------------------------------|-----------------|--------------------------------|-----------------|--------------------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------------------------|-----------------------------------------------------------|
| Feed type | Cellulose | Cellulose | Cellulose | Cellulose | Cellulose | Cellulose | Cellulose | Cellulose |
| Feed (g) | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 |
| Catalyst | K ₂ CO ₃ | Na ₂ | K ₂ CO ₃ | Na ₂ | 5% Pt/Al ₂ O ₃ + K ₂ CO ₃ | 5% Pt/Al ₂ O ₃ + Na ₂ | 5% Pt/Al ₂ O ₃ + K ₂ CO ₃ | 5% Pt/Al ₂ O ₃ + Na ₂ |
| Catalyst (g) | 1.0 | 1.0 | 1.0 | 1.0 | 5+5=1.0 | 0.5+0.5=1.0 | 0.5+0.5=1.0 | 0.5+0.5=1.0 |
| Water, g | 400.0 | 400.0 | 400.0 | 400.0 | 400.0 | 400.0 | 400.0 | 400.0 |
| Reducing gas | H ₂ | H ₂ | CO | CO | H ₂ | H ₂ | CO | CO |
| Reducing gas (g) | 1.6 | 1.6 | 22.12 | 22.12 | 1.6 | 1.6 | 22.12 | 22.12 |
| TOTAL INPUT (g) | 452.6 | 452.6 | 473.12 | 473.12 | 452.6 | 452.6 | 473.12 | 473.12 |
| Temperature (°C) | 300 | 300 | 300 | 300 | 300 | 300 | 300 | 300 |
| Initial pressure (atm) | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 |
| Heating up time (hr) | 1.40 | 1.50 | 2.30 | 2.35 | 2.0 | 2.10 | 2.30 | 2.20 |
| Reaction time (hr) | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Max. Reaction press(atm) Final | 280 | 280 | 290 | 285 | 295 | 292 | 310 | 300 |
| Reaction press (atm) | 37 | 36 | 40 | 38 | 40 | 44 | 38 | 36 |
| TOTAL OUTPUT (g) | 451.0 | 450.7 | 471.4 | 471.8 | 450.9 | 450.9 | 472.0 | 471.82 |
| % Recovery from Autoclave | 99.6 | 99.6 | 99.64 | 99.72 | 99.6 | 99.6 | 99.8 | 99.72 |
| Product Distribution | | | | | | | | |
| % Gas produced | 16.0 | 11.56 | 18.76 | 28.8 | 12.8 | 15.96 | 31.76 | 26.40 |
| % Water-soluble fraction | 12.6 | 8.6 | 6.8 | 8.6 | 12.4 | 5.60 | 3.00 | 10.40 |
| % Oil | 17.6 | 40.0 | 38.6 | 21.2 | 24.4 | 40.0 | 50.00 | 20.60 |
| % Char | 19.0 | 8.0 | 6.4 | 14.6 | 12.0 | 7.0 | 3.00 | 11.00 |
| % Water-produced | 31.6 | 28.0 | 26.0 | 24.2 | 35.0 | 28.0 | 10.00 | 29.00 |
| % TOTAL RECEIVED | 96.8 | 96.76 | 96.56 | 97.4 | 96.6 | 96.56 | 97.76 | 97.4 |
| % CONVERSION | 75.64 | 89.59 | 92.28 | 78.9 | 78.68 | 93.73 | 96.94 | 81.44 |

Table 2. Elemental analysis

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| Feedstock analysis | | | | | | | | |
| % C | 41.5 | 41.5 | 41.5 | 41.5 | 41.5 | 41.5 | 41.5 | 41.5 |
| % H | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 |
| % O* | 52.4 | 52.4 | 52.4 | 52.4 | 52.4 | 52.4 | 52.4 | 52.4 |
| % Ash | - | - | - | - | - | - | - | - |
| Char analysis | | | | | | | | |
| % C | 53.2 | 54.0 | 50.0 | 60.0 | 73.7 | 52.0 | 42.2 | 70.0 |
| % H | 4.9 | 4.5 | 3.9 | 5.5 | 4.6 | 4.2 | 4.0 | 4.2 |
| % O* | 28.0 | 15.0 | 12.0 | 23.7 | 21.7 | 8.9 | 6.8 | 10.8 |
| % Ash | 13.9 | 26.5 | 34.1 | 10.8 | | 34.9 | 47.0 | 15.0 |
| Oil analysis | | | | | | | | |
| % C | 75.6 | 77.8 | 78.0 | 68.9 | 78.0 | 74.5 | 75.3 | 73.9 |
| % H | 6.5 | 7.2 | 7.5 | 6.1 | 7.0 | 7.6 | 8.0 | 6.8 |
| % O* | 17.9 | 12.2 | 11.0 | 13.3 | 15.0 | 9.8 | 9.5 | 12.0 |
| % Ash | - | 1.0 | 3.5 | 11.7 | | 8.1 | 7.2 | 7.3 |
| H/C | 1.02 | 1.10 | 1.14 | 1.05 | 1.07 | 1.21 | 1.26 | 1.09 |
| O/C | 0.177 | 0.117 | 0.10 | 0.146 | 0.144 | 0.098 | 0.094 | 0.146 |
| Caloric value (Kcal/g) | 7.5320 | 8.6512 | 8.6923 | 8.2513 | 8.3520 | 8.7215 | 8.7580 | 8.5571 |

Table 3. Product oil composition

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|----------------------------------|------|------|------|------|------|------|------|------|
| Product oil composition | | | | | | | | |
| % Heptane soluble Lights. | 35.8 | 50.2 | 55.0 | 38.3 | 41.6 | 61.2 | 63.5 | 46.7 |
| % Heptane soluble (boil), Waxes. | 8.90 | 13.4 | 14.8 | 12.3 | 12.0 | 13.8 | 15.0 | 12.3 |
| % Toluene soluble Asphaltenes. | 33.0 | 22.7 | 20.2 | 31.2 | 28.9 | 17.0 | 15.0 | 25.8 |
| % Toluene insoluble, Resins. | 22.3 | 13.7 | 10.0 | 18.2 | 17.5 | 8.0 | 6.5 | 15.2 |

Table 4. Extraction of different functional group(compounds) from ether soluble fraction of water soluble fraction.

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--------------------------------------|-------|------|------|------|------|------|------|------|
| % Ether soluble fraction (from WSF*) | 40.0 | 27.0 | 25.0 | 32.0 | 36.0 | 22.0 | 20.0 | 28.0 |
| % A | 14.2 | 9.0 | 8.5 | 9.6 | 10.2 | 7.0 | 6.4 | 9.0 |
| % B | 9.2 | 6.5 | 6.2 | 8.0 | 8.8 | 5.0 | 4.0 | 6.8 |
| % C | 4.5 | 2.2 | 2.5 | 2.0 | 4.0 | 2.0 | 3.0 | 1.6 |
| % D | 8.4 | 8.2 | 7.0 | 8.5 | 8.6 | 6.4 | 5.2 | 7.5 |
| % E | 2.2 | 0.6 | 0.5 | 1.5 | 2.8 | 1.0 | 0.6 | 1.1 |
| % Total | 38.5 | 26.5 | 24.7 | 29.6 | 34.4 | 21.4 | 19.2 | 26.0 |
| % Recovery | 96.25 | 98.0 | 98.8 | 92.5 | 96.0 | 97.0 | 96.0 | 93.0 |

A - Carboxylic acids (extracted by aqueous 10% Na_2CO_3 solution).

B - Heavy carboxylic acid

C - Carbonyl compounds (extracted by aqueous 5% NaHSO_4 solution).

D - Phenolic compounds (extracted by aqueous 10% NaOH solution).

E - Neutral hydrocarbons (etheral soluble compounds).

* WSF - Water soluble fraction

** All percentages are w/wt of ether soluble fraction

*** % of ether soluble fractions were obtained from Water soluble fraction by treating with di-ethyl ether.

Table 5. Product of gas distribution

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------------------------------|--------|-------|-------|-------|-------|-------|-------|-------|
| % CO | 42.64 | 37.95 | 31.09 | 29.86 | 46.84 | 36.84 | 25.97 | 38.55 |
| % CO_2 | 24.21 | 24.68 | 52.25 | 50.09 | 25.06 | 40.26 | 61.04 | 50.90 |
| % CH_4 | 3.81 | 2.76 | 2.91 | 3.16 | 2.91 | 3.01 | 2.82 | 2.84 |
| % C_2H_6 | 0.59 | 0.57 | 0.59 | 1.02 | 0.60 | 0.59 | 0.63 | 0.65 |
| % C_2H_4 | 0.83 | 0.55 | 0.58 | 1.04 | 0.72 | 0.68 | 0.71 | 0.61 |
| % C_3H_8 | 1.14 | 0.71 | 0.66 | 1.09 | 0.85 | 0.55 | 0.81 | 0.67 |
| % C_3H_6 | 0.23 | 0.24 | 0.18 | 0.27 | 0.26 | 0.21 | 0.24 | 0.16 |
| % n-Butane | - | - | - | - | - | - | - | - |
| % 1-Butene | - | - | - | - | - | - | - | - |
| % iso-butene | - | - | - | - | - | - | - | - |
| % Trans-2-butene | 1.31 | 1.50 | 1.37 | 1.35 | 1.53 | 1.46 | 1.26 | 0.93 |
| % Cis-2-butene | 0.87 | 0.42 | 0.89 | 0.85 | 0.88 | 1.05 | 0.83 | 0.61 |
| % Butadiene | 1.72 | 2.09 | 1.75 | 1.70 | 1.72 | 1.86 | 1.72 | 0.85 |
| % Total | 77.35 | 71.47 | 92.27 | 90.43 | 81.37 | 86.51 | 87.04 | 96.77 |
| % H_2 + UP* [†] | 22.655 | 28.53 | 7.73 | 9.57 | 18.63 | 13.49 | 12.96 | 3.23 |

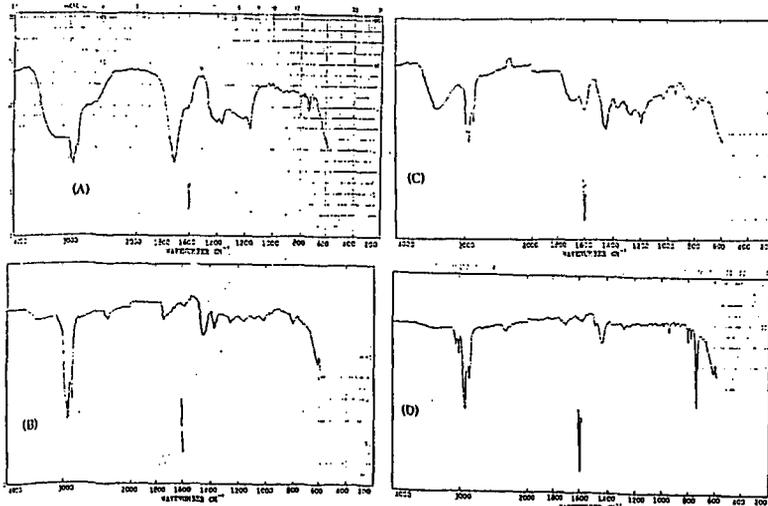


Figure 1A. IR spectra of aqueous extracts: (A) Na_2CO_3 extract (B) NaHSO_4 . Figure 2A. IR spectra of aqueous extracts: (C) NaOH extract (D) Etheral-soluble.

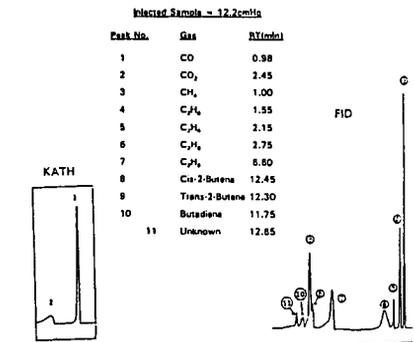
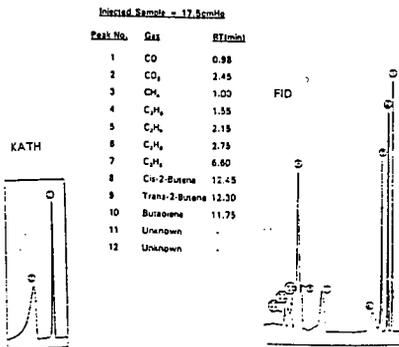
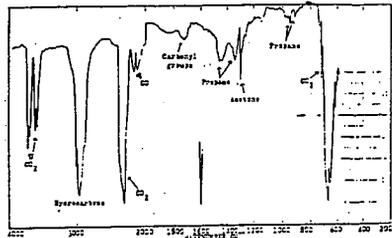
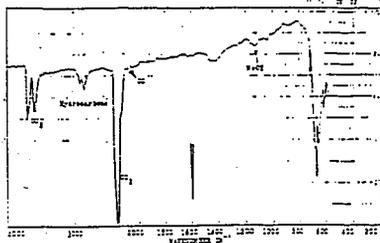


Figure 4A.

Figure 5A. The IR spectrum and GC chromatograms of the gaseous product from run 5

The IR spectrum and GC chromatograms of the gaseous product from run 6.

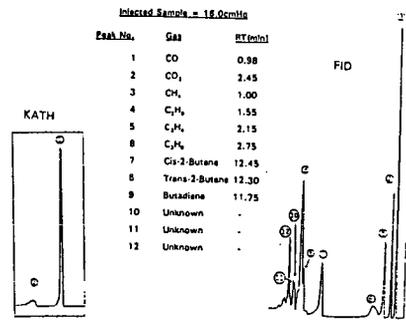
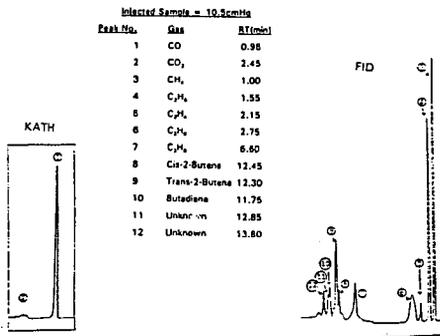
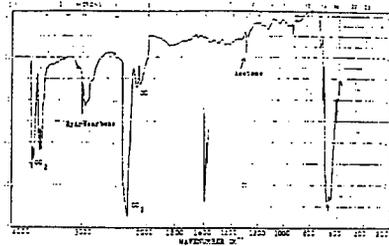
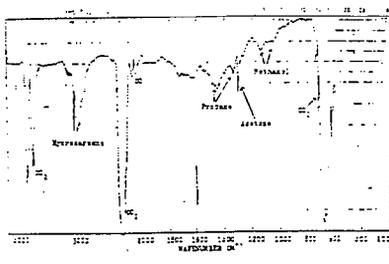


Figure 6A.

Figure 5A. The IR spectrum and GC chromatograms of the gaseous product from run 7.

The IR spectrum and GC chromatograms of the gaseous product from run 8