

## Synthesis of Methyl Alcohol and Alternative Gases for Petroleum by Thermochemical Gasification of Waste Lignocellulosic Materials ( I )

--- Thermochemical Conversion of Sawdust, Ricestraw and Ricehusk  
Using Alkali Salts as Catalyst --- \*1

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木質廢材의 熱-化學的 方法에 의한 메틸알콜과 代替에너지 가스의 合成(I)  
--- 알칼리염을 촉매로 사용한 톱밥, 볏짚 그리고 왕겨의 熱化學的 分解 --- \*1

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### 要 約

木質物質인 톱밥, 볏짚 그리고 왕겨를 熱分解하여 氣相物質을 合成하기 위해, 석영으로 설계 제작된 反應塔을 사용하였다. 최초의 반응온도 350℃로 부터 熱分解와 gasification 反應이 完結된다고 豫상되는 550℃까지 가열하였다.

촉매가 반응온도에 어떤 영향을 미치는지 조사하기 위해  $K_2CO_3$  와  $Na_2CO_3$  를 촉매로 사용하였다.

合成 gas 는 gas chromatograph 와 mass spectrometer 에 의해  $CO$ ,  $CO_2$ ,  $CH_4$  그리고  $CH_3CHO$  등인 것으로 判明되었다. 合成 gas 의 收率과 組成은 反應溫度와 이 반응에 사용되는 촉매에 달려있지만, 톱밥을 試料로 반응온도 550℃,  $K_2CO_3$  를 촉매로 사용한 反應에서 生成되는 gas 體積은 1,800 ml/g 톱밥에 달한다.

### Summary

A quartz type gasification reactor was designed and used for pyrolysis and gasification of sawdust, ricestraw and ricehusk. The initial reaction temperature was 350°C, and up to 550°C to complete pyrolysis and gasification reaction. In order to examine the effect of catalyst on reaction temperature,  $K_2CO_3$  and  $Na_2CO_3$  as catalyst were also used.

The product gas mixtures are identified to be  $CO$ ,  $CO_2$ ,  $CH_4$  and  $CH_3CHO$  etc. by Gas Chromatography and Mass Spectrometer.

The highest gas volume of the gasified sawdust at 550°C amounts to 1800ml/g of sawdust, even though the yield and composition of this product gas are depending on the reaction temperature of the reactor and catalyst used.

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## 1. Introduction

The studies of thermochemical conversion of biomass to fuels or other alternative natural resources have been extensively worked, since Robert Mudoch introduced his pyrolyzing technology (1) of wood and wood residues for the first time in 1792.

Either gasification or pyrolysis of carbonaceous materials produces a mixture of gaseous products as a result of the complex, parallel, competitive and sequential chemical reactions occurring. The preferred reactions, i.e., those which produce the most desirable products, are limited and slow at conventional processing temperatures. However, the rates can be enhanced by inclusion of certain catalysts. Furthermore, a variety of catalysts, reaction temperature and steam partial pressure will be used industrially to promote certain reactions to emphasize formation of desired products from other gas mixtures.

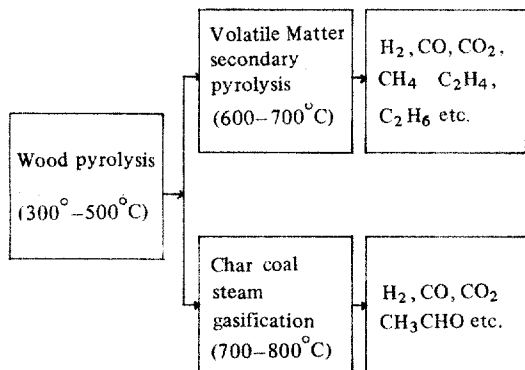


Figure 1. A possible scheme of wood gasification process.

### 1.1 General Behavior of Wood Gasification

The general behavior of wood gasification process is illustrated in Figure 1 which are three steps, (1) pyrolysis, producing volatile matter and char; (2) secondary reactions of the evolved volatile matter in the gas phase; and (3) char gasification via steam char reaction (2, 3, 4).

Pyrolysis of biomass materials occurs under normal conditions at relatively low temperatures (300° to 500°C), producing volatile matter and

char. Very rapid heating causes pyrolytic weight loss to occur at somewhat higher temperatures. In general, the volatile matter content of cellulosic materials approximates 80% of the dry weight of the initial feedstock. Woody materials contain between 60% and 70% volatile matter, and manures contain 50% volatile matter.

Volatile matter produced by pyrolysis of wood begins to participate in secondary gas phase reactions at temperatures exceeding 600°C. These reactions occur very rapidly and yield a hydrocarbon rich syngas product. As recognized by Diebold (5), these reactions resemble the hydrocarbon cracking reactions employed in the manufacture of ethylene and propylene by the petrochemical industry (6, 7). The secondary gas phase reactions dominate the gasification chemistry of biomass.

At still higher temperatures (>700°C) pyrolytic char reacts with steam to produce hydrogen, carbon monoxide and carbon dioxide. Rates of gasification of biomass derived chars are known to be higher than coal derived chars (8); however much higher temperatures are required to achieve char gasification than were initially required for the pyrolysis reactions. Catalysis of char gasification has been reported (9, 10) with limited success.

### 1.2 Pyrolysis of Wood Components

Incipient decomposition takes place at temperatures slightly above 100°C. From 200°C upwards the decomposition of hemicellulose and lignin becomes appreciable and above 250°C, xylan decomposes very rapidly. The behavior of glucomannan in all likelihood parallels that of xylan. The reactions at this point are often very violent and accompanied with the production of pyrolysis gas, water and volatile organics. Afterwards, these reactions gradually subside. Cellulose remains essentially stable until 350°C where a rapid decomposition sets in. At about 400°C, the carbohydrate constituents have been largely converted to volatile products while about one half lignin still remains in the solid residue. Consequently, lignin is the major source of charcoal (8-14).



Alkali carbonates also have an effect upon the products obtained during biomass gasification. This is thought to be due to their re-direction of volatilization pathways (24, 25, 26) as well as their catalysis of the water-gas shift reaction, which has been reported elsewhere (27). Nickel catalysts, such as the commercial supported nickel methanation catalyst employed in this research, are also believed to alter volatilization pathways. As a result, the use of mixtures of alkali and nickel catalysts in the gasification of biomass or other carbonaceous material (28) has a large effect upon the product gas composition. This, in turn, can greatly improve the energy yield which can be obtained via biomass gasification.

## 2. Experimental

### 2.1 Materials

As raw materials, ricestraw, ricehusk and sawdust are used for this gasification matter.  $N_2$  gas is also used for an inert gas in the quartz type gasification reactor.  $K_2CO_3$  and  $Na_2CO_3$  are used as catalyst.

### 2.2 Method

The continuous-feed, fixed-catalyst bed reactors constructed of quartz glass were used for these studies. The reactors, which were operated at atmospheric pressure are shown in Figure 3. The raw materials such as ricestraw, ricehusk and sawdust is fed into the top of the reactors at a rate of 10-15 g/hr and gasified in the presence of steam. The volatile material passes over a bed of catalyst in the bottom of the reactor. The space velocity over the catalyst is typically 800-1500  $cm^3/g$  catalyst/hr. Char and ash accumulate on a support just above the catalyst bed and are vacuumed out periodically.

Analytical equipment used with the laboratory gasification system includes Hitachi Mo. No. 163 analytical gas chromatograph for gas analysis, a Hewlett Packard 125 gas chromatograph mass

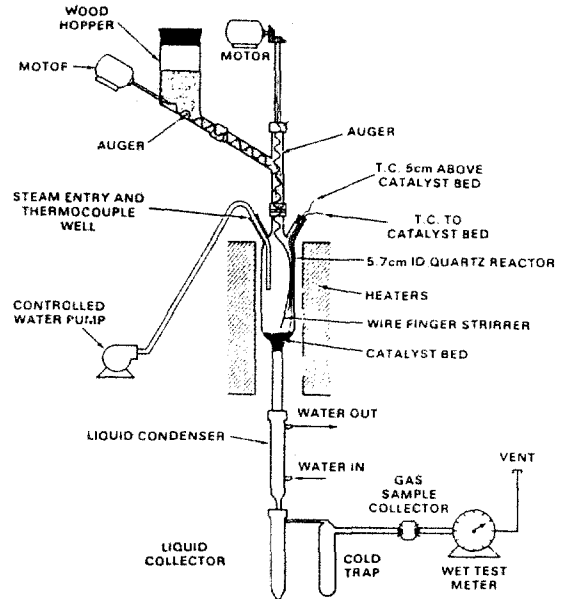


Figure 3. The continuous-feed, fixed-catalyst bed reactor used for this project.

spectrometer for the molecular structures of the gasified fragmentation. Other analytical equipment was used for special purposes and will be discussed where appropriate.

## 3. Results and Discussion

### 3.1 The Factors Affecting on Gas Yield

The Figure 4 shows the effect of gasifying temperature on gas yield of sawdust as feedstock. In this figure gas yield is increasing with increasing pyrolysis temperature. The gas volume of the various kind of gas mixtures amounts to 1800 ml/g wood within 30 minutes of gasifying time of 550°C.

The Figure 5 shows the effect of catalyst on gas yield of ricestraw as feedstock.  $K_2CO_3$  and  $Na_2CO_3$  are used as catalyst in this work. Both alkali salts are experienced to be most effective catalyst for lignocellulose gasification in the other's research works (20-28). Of this two selected catalysts,  $K_2CO_3$  is an apparently better catalyst than  $Na_2CO_3$  in terms of gasifying effects in Figure 5.

Figure 6 indicates the effect of feedstocks on

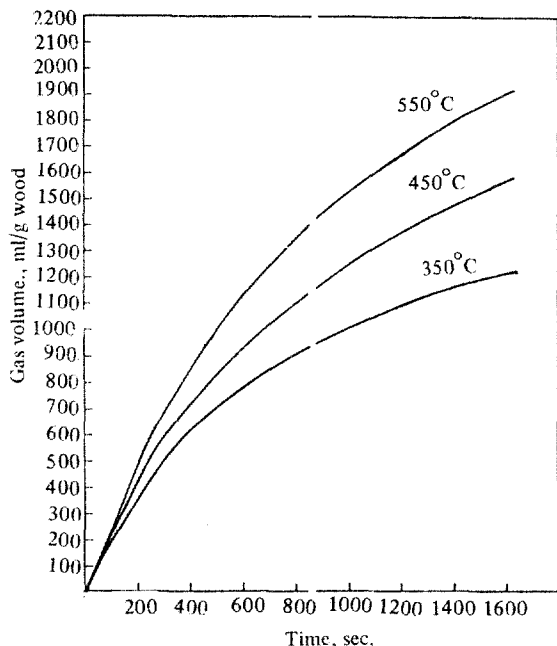


Figure 4. Effect of temperature on gas production.

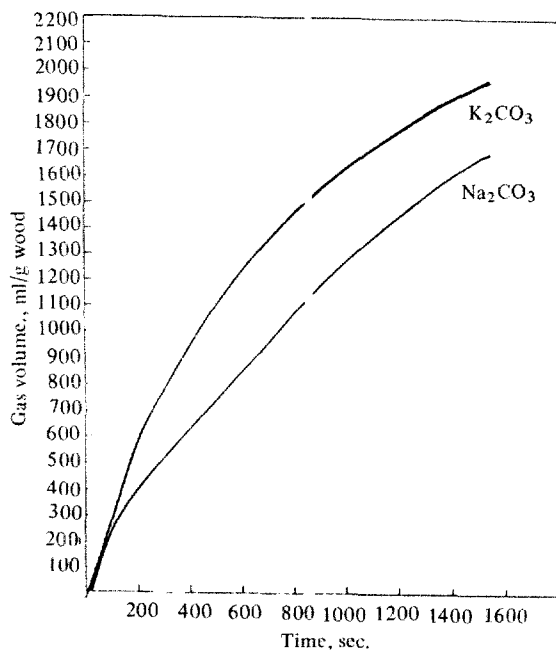


Figure 5. Effect of catalysts on gas production.

gas yield. In this figure, sawdust as feedstock is appeared to be most producible material of the three feedstocks for this thermochemical conversion of lignocellulosic materials.

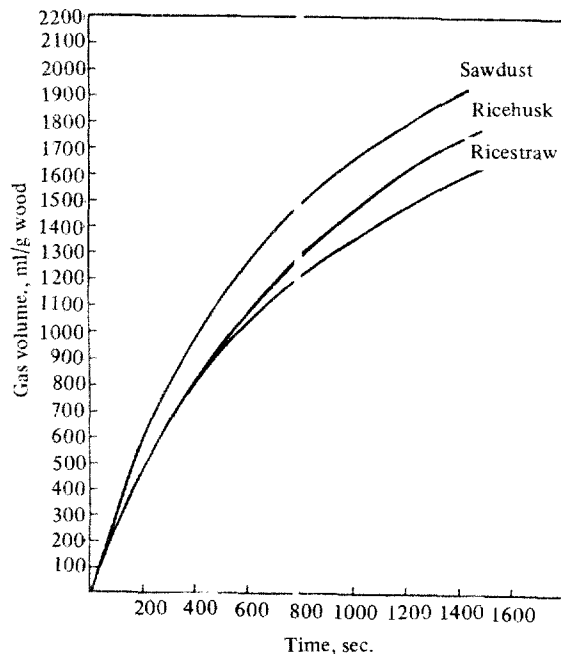


Figure 6. Effect of raw materials on gas production.

### 3.2 Pyrolysis Spectra of Lignocellulosic Materials

The primary pyrolysis of cellulose has been extensively studied by Shafizadeh and his coworkers (29) and their cumulative work is of much help in interpreting the spectrum for cellulose shown in Figure 7 and 8. The striking simplicity of cellulose pyrolysis, particularly in the higher mass region, is an indication of the dominance of the transglycosylation mechanism that leads to levoglucosan formation. Interpretation performed by them (29) indicates that the major product is levoglucosan at  $m/z$  162 despite the small peak size. The peak at  $m/z$  324 is believed to be due to a dimer of levoglucosan and similar multiples of 162 are observed out to  $m/z$  1400. The peak at  $m/z$ 's 163 and 325 are believed to be fragment ions of these higher oligomers.

Especially Figure 8 shows (29) that the addition of catalytic amounts of alkali salts to cellulose has been shown to inhibit levoglucosan formation (29). It is the primary pyrolysis spectrum of cellulose treated with 5%  $K_2CO_3$  (mole) solution.

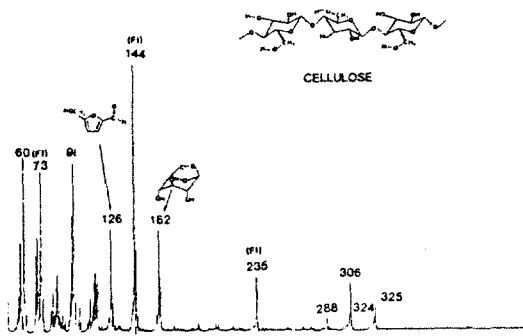


Figure 7. GC-spectra of pyrolysis products of cellulose.

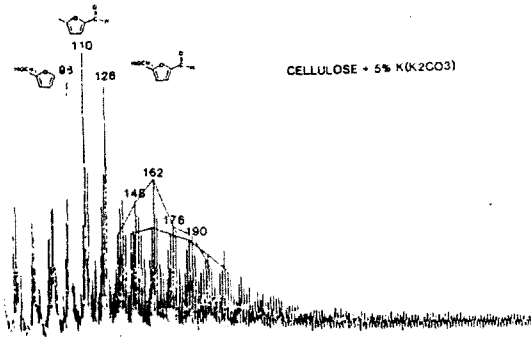


Figure 8. GC-spectra of cellulose treated with 5%  $K_2CO_3$ .

It is shown that the simplicity of cellulose pyrolysis has been replaced by a much more complicated spectrum with the noticeable absence of levoglucosan and the dimer. In this Figure, they (29) indicate that the masses associated with furan compounds are now predominant:  $m/z$  98, furfuryl alcohol;  $m/z$  110, 5-methylfurfural; and  $m/z$  126, 5-(hydroxy-methyl)-furfural.

Figure 9 is the GC-mass spectra of pyrolysis products of sawdust using the reactor shown in Figure 3. The pyrolysis temperature was  $450^\circ C$ . Figure 10 is also the GC-mass spectra of its using same reactor. But the pyrolysis temperature was  $550^\circ C$ .

Comparing the result shown in Figure 10 with that shown in Figure 9, it shows an apparent difference in terms of pyrolysis products. From both spectra, it is identified that  $CH_4$  gas is produced.

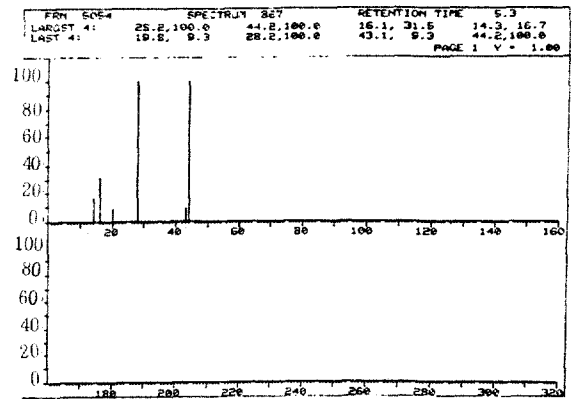


Figure 9. GC-mass spectra of the primary pyrolysis ( $450^\circ C$ ) products of sawdust.

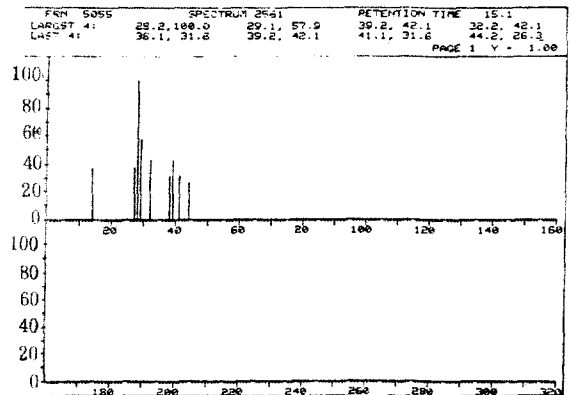


Figure 10. GC-mass spectra of the primary pyrolysis ( $550^\circ C$ ) products of sawdust.

But the peak at  $m/z$  44 in Figure 10 is not appeared at Figure 9, which is identified as  $CH_3CHO$ . Two or three other pyrolysis products unidentified, which is shown in Figure 10 are not appearing in Figure 9. From this results, it can be predicted that higher pyrolysis temperature is more effective in terms of not only gas volume but also sort of the produced.

#### 4. Conclusions

This is the first report of the thermochemical conversion of biomass project. So it is very difficult

to have a conclusion of this technology using sawdust, ricestraw and ricehusk as feedstock. However even if this experimental result is a beginning report of a long way to go, it is shown that the thermo-chemical conversion effects of the catalyst and pyrolysis temperature are apparently indicative as seen in Figures of this paper and unexpressed experimental results.

The higher pyrolysis temperature shows higher product gas volume and more variety of gas produced.

The catalysts using alkali salts are also apparently effective to increase gas volume produced, as seen in Figure 5. From this conclusions, the future and further study of this thermochemical conversion of biomass will direct to find out the more effective catalyst in terms of gas volume and the variety of gas produced, because to increase gas volume and to decrease pyrolysis temperature by catalyst is most desirable and economic in such countries as Korea in which the cost of heat energy is so expensive.

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