⬆EPA   # Project Summary

Evaluation of Biomass Reactivity in Hydrogasification for the Hynol Process

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The reactivity of poplar wood in hydrogasification under the operating conditions specific for the Hynol process was evaluated, using a thermobalance reactor. Parameters affecting gasification behavior, e.g., gas velocity, particle size, system pressure, reaction temperature, reaction time, and feed gas composition, were investigated. The experimental results showed that temperature and particle size strongly affect biomass conversion and gasification rates. The poplar wood conversion is proportional to the partial pressures of hydrogen and steam in the feed gas. A conversion of 86-87% was observed when 1/8-in. (0.32 cm) poplar particles were gasified at 30 atm (2942 kPa) and 800°C for 60 min with the feed gas composition simulating the Hynol recycled gas from the methanol synthesis reactor. As the reaction time extended to 2.5 hours, the conversion increased to 90%. It was found that gasification involves a rapid reaction of biomass thermal decomposition and a slow reaction of residual carbonaceous matter with the feed gas. The activator energies for these reactions were estimated. A kinetic model was developed to quantitatively express gasification rates and biomass conversion as functions of reaction time. The model was used to correlate the thermobalance reactor experimental data. The carbon, hydrogen, and oxygen contents in the charred samples obtained after different gasification times were analyzed and compared. Potassium carbonate was found to catalyze biomass gasification and increase the carbon conversion of poplar wood.

The gasification reactivity of pressed switchgrass was briefly evaluated.

This Project Summary was developed by EPA's National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Hynol process was proposed to meet the increasing demand for economical production of methanol from biomass and natural gas. The process consists of three reaction steps: (1) hydrogasification of biomass with the recycle gas remaining after methanol synthesis, (2) steam reforming of the produced gas with addition of natural gas feedstock, and (3) methanol synthesis from the hydrogen (H_2) and carbon monoxide (CO) produced. These three reactions take place in the hydropyrolysis reactor (HPR), the steam pyrolysis reactor (SPR), and the methanol synthesis reactor (MSR), respectively.

After theoretical evaluation, the U.S. Environmental Protection Agency's Air Pollution Prevention and Control Division (APPCD) concluded that the Hynol process represents a promising technology for maximizing fuel production inexpensively and with minimum greenhouse gas emissions. Under contract to APPCD, Acurex Environmental Corporation has established laboratory research facilities to perform supporting kinetic studies of two principal reactions of the Hynol process: biomass hydrogasification and meth-

ane steam reforming. The studies are aimed at improving understanding of these reactions, providing quantitative information to support the design and operation of a bench-scale evaluation, and identifying additional needs for Hynol process development.

A thermobalance reactor (TBR) has been installed to evaluate biomass reactivities in hydrogasification under the operating conditions specific for the Hynol process. The report summarizes the TBR test results.

Experimental

Figure 1 is a flow diagram of the test facility. The TBR used in the study is electrically heated and consists of a 35-mm stainless steel reaction pipe, a pressure vessel, and a topwork which accommodates a weight transducer for measuring sample weight during reaction. To initiate an experimental run, a basket with known weight of the biomass sample was charged into the topwork through the window gauge. Mass flow controllers were used to control the flow rates of hydrogen, methane (CH_4), carbon monoxide, and carbon dioxide (CO_2) to maintain the desired feed gas composition. The mixed gas was preheated to 350°C by electric heat tracing. A high performance liquid chromatography (HPLC) pump was used to meter and inject distilled water (H_2O) from a reservoir into the gas line where the H_2O was vaporized by the preheated feed gas. The gas was then preheated to the desired
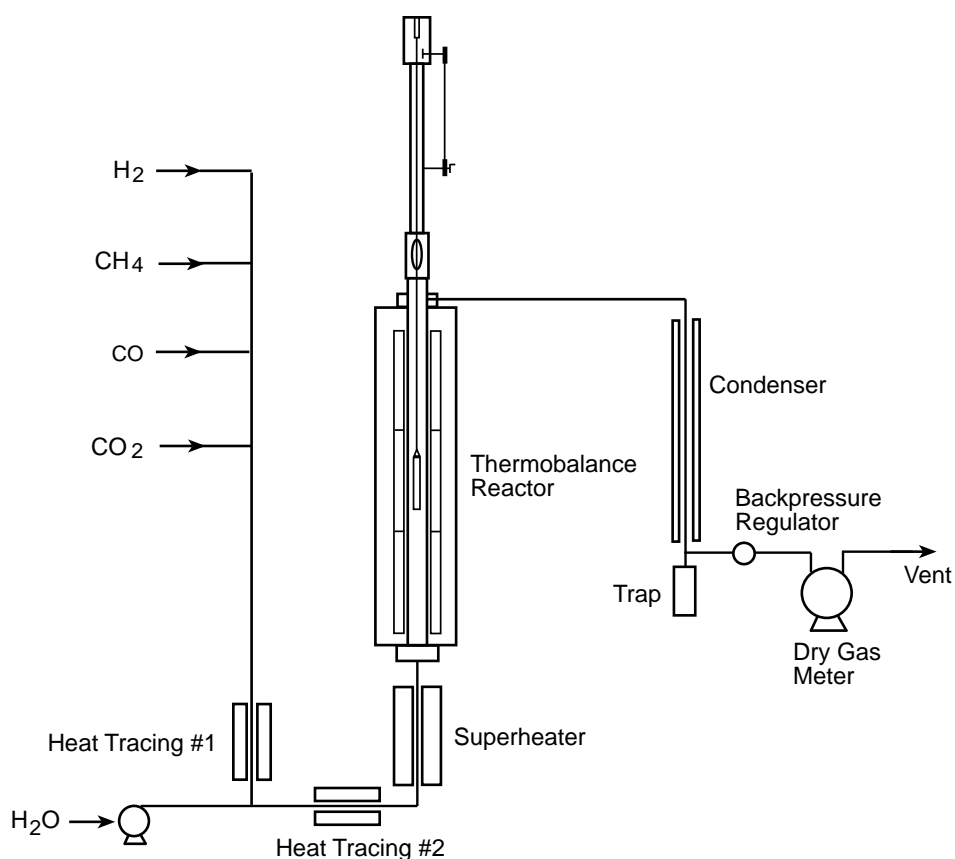

Figure 1. Flow diagram of the thermobalance reactor (TBR) system

operating temperature in the lower part of the reactor. The exit gas from the TBR was cooled in a condenser to remove moisture, and then passed through a high pressure filter and a backpressure regulator before it was vented to atmosphere. When pressure and temperature were stabilized at the desired levels, the sample basket was lowered into the reaction zone and the changes in sample weight were automatically recorded by the transducer as a function of reaction time. Because the change in gas composition across the sample is negligible, the reactions can be considered to take place at constant conditions. A personal computer, equipped with LabTech software, was used to control the TBR facility and log experimental data.

Poplar wood grown in North Carolina was used as the representative biomass sample. It was cut to the desired size and dried before use. A few tests were also conducted with pressed switchgrass. The compositions of poplar wood and switchgrass used are presented in Table 1.

The reactivities in hydrogasification were evaluated under the Hynol operating conditions based on the results of the Hynol process simulation provided by the EPA, in which the biomass is hydrogasified at 30 atm (2942 kPa) and 800 °C and with a feed gas composition: H_2 = 65.83%, CH_4 = 11.63%, CO = 8.95%, CO_2 = 2.32% and H_2O = 11.27%. Effects of deviation from these operating conditions were also investigated.

Kinetic Model and Data Treatment

In data treatment, the changes in sample weight recorded by the weight transducer were transformed to biomass conversion as a function of reaction time. Biomass conversion is defined on an ash-free basis and can be calculated from the recorded variation in sample weight by:

$$X = (W_0 - W) / (W_0 - W_0 C_A) \qquad (1)$$

where W_0 = Initial sample weight

W = Recorded sample weight at time t

C_A = Ash content in the sample analyzed from the ultimate analysis.

The carbon conversion is equal to the amount of carbon gasified divided by the amount of carbon in the initial biomass sample and can be calculated from the carbon contents in the sample analyzed before and after gasification as:

$$\alpha = 1 - W_{CF}/(W_0 C_C) \qquad (2)$$

where W_{CF} = Weight of the carbon remaining in the char after gasification

C_C = Carbon weight fraction in biomass sample before gasification

When the analysis of carbon content in a charred sample is not available, an approximate carbon conversion can be estimated by assuming that all hydrogen and oxygen in the biomass sample are converted into a gas product after gasification and the residual char contains only carbon and ash. Thus, the carbon conversion is approximated as a function of the biomass conversion by:

$$\alpha = 1 - (1 - X)(1 - C_A) / C_C \qquad (3)$$

To quantitatively evaluate biomass reactivity and gasification rate, a kinetic model has been developed. The following assumptions were made in model development:

(a) Two types of reactions involved in biomass hydrogasification can be classified in terms of mechanism and reaction rate: the thermal decomposition reaction of biomass and the reaction of residual carbonaceous matter with process gas. The former reaction is rapid and may be completed in seconds, while the latter is very slow and requires hours to finish.

(b) Both reactions are first order with respect to the remaining solid reactants and can be expressed by:

$$dX_1 / dt = K_1 (X_C - X_1) \qquad (4)$$

and

$$dX_2 / dt = K_2 (1 - X_C - X_2) \qquad (5)$$

Table 1. *Analysis Results of Poplar Used in this Study and Comparison with Other Reported Data*

Sample	Poplar	Poplar	Poplar	Switchgrass
Data Source	This Study	BNL*	Noyes**	This Study
Carbon wt.%	51.52	51.32	51.60	47.39
Hydrogen	6.20	6.16	6.30	6.15
Oxygen	41.37	34.57	41.50	40.09
Ash	0.47	6.64	0.60	5.07
Sulfur	0.02	0.13	0	0.06
Nitrogen	0.42	1.18	0	1.22
Volatile	91.38			76.97
Fixed Carbon	8.15			17.96
Higher Heating Value (Btu/lb) Moisture Free Basis	8768	7861	8920	7836

* Brookhaven National Laboratory
** Noyes Data Corporation

where X_1 and X_2 are the conversions by the rapid and slow reactions, respectively; X_C is the maximum fraction of the matter convertible by the rapid reaction; and K_1 and K_2 are the reaction rate constants for the rapid and slow reactions. By integrating Equations (4) and (5), the total biomass conversion can be expressed as:

$$X = 1 - X_C \exp(-K_1 t) - (1-X_C) \exp(-K_2 t) \quad (6)$$

From Equation (6), the conversion is zero at $t = 0$ and would approach 1 as t approaches infinity. The model has three parameters: X_C, K_1, and K_2, which are functions of sample properties and reaction conditions, and can be determined by correlating the data of conversion versus reaction time obtained from the TBR experiments.

Results and Discussion

Model Prediction

The applicability of the developed model to the biomass hydrogasification under the Hynol operating conditions was investigated. Figure 2 shows good agreement between the experimental data and the model regression curve over a period of 60 min, indicating that the model can be used to correlate the TBR experimental data and quantitatively express the variation in gasification rate as a function of time. By correlating the 60-min gasification data obtained with 1/8-in. poplar particles at 30 atm and 800°C, the model parameters determined were $X_C = 0.8405$, $K_1 = 18.3$ min^{-1}, and $K_2 = 0.0035$ min^{-1}.

Substituting these parameters into Equation (6), the conversions at other gasification times were predicted. The calculated conversions, X_{cal}, were then compared to the results, X_{exp}, obtained from the separate experimental tests for various gasification times, as shown in Figure 3. The maximum relative error in the comparison is 1.7%. The comparison covers a range of reaction time from 0.2 to 150 min.
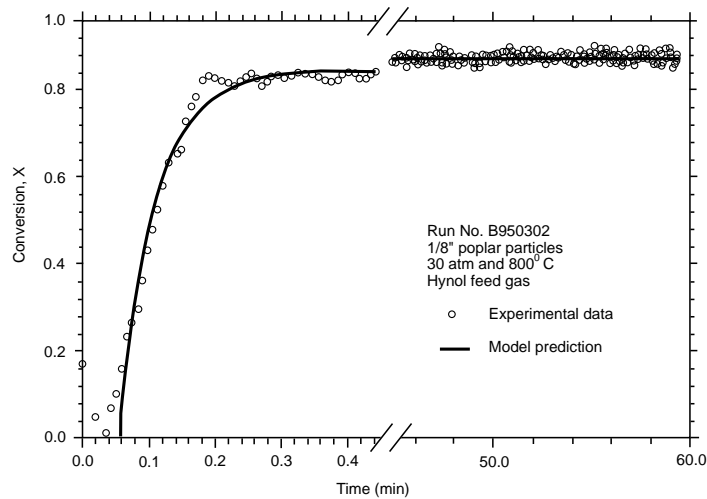

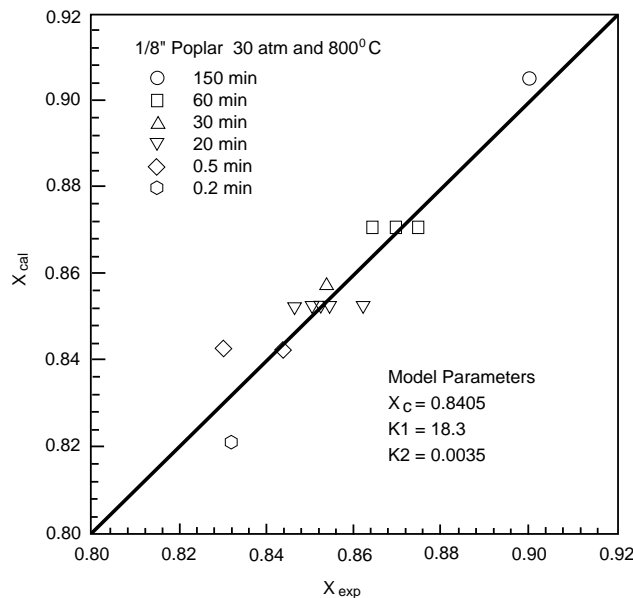**Figure 2**. *The comparison of experimental conversion data with the model correlation results*

Figure 3. *Comparison of the experimental data from the separate tests with the model predictions (reaction temperature = 800°C)*

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Effects of Particle Size

Four sizes of poplar particles used to investigate the effects on gasification were 7/16-in. (1.1 cm) diameter cylinders, 1/4-in. (0.64 cm) diameter cylinders, 1/8-in. (0.32 cm) cubes and 20 - 30 mesh sawdust. It was found that the rate of the rapid reaction increased significantly as a result of the rate increase in heat transfer and intraparticle diffusion when particle size was reduced from 7/16 to 1/8 in. The sawdust showed the highest conversion. Agglomeration during gasification was observed for the poplar particles 1/8 in. or larger, which reduced the gas diffusion within the particles.

The chars obtained by gasifying different sizes of poplar particles were analyzed. Some of the volatile matter remained in the residual chars after 30 min gasification of 7/16-in. poplar particles. However, nearly all of the hydrogen and oxygen in 1/8 in. poplar and sawdust were converted in 20 min. The residual cooled, chars after gasification are fragile and can be easily ground to fines by attrition.

Effects of Biomass Residence Time

The experiments showed that the rapid reaction stage for 1/8 in. poplar particles could be essentially completed in less than 0.2 to 0.3 min, converting most of the biomass into gas product. The conversion contributed by the slow reaction is relatively small and proceeds very slowly. At 30 atm and 800°C, 84% of 1/8-in. poplar was converted by the rapid reaction, and the slow reaction converted an additional 3% in 60 min.

To achieve high biomass conversion, sufficient biomass residence time must be provided. It was found that an additional 10% biomass conversion could be obtained when the reaction time extended from 20 to 150 min. The composition comparison between the charred samples after 20 and 150 min gasification indicated that there was virtually no hydrogen and oxygen in the char after 20 min. The additional conversion after 20 min was contributable to the carbon reactions.

With an estimated residence time of 7.86 h for the bench-scale gasifier, it was predicted that 94% of the total dry biomass or 88% of the biomass carbon content can be converted in the Hynol gasification.

Effects of Temperature

To investigate the effects of reaction temperature, the experiments were conducted at five temperature levels: 750, 800, 850, 900, and 950°C. In these tests 1/8-in. poplar particles were exposed to the simulated Hynol feed gas at 30 atm pressure. The gasification time was 60 min for these tests to identify the conversion contribution of the slow reaction at high temperatures. Conversion increased as temperature was raised from 800 to 900 °C as shown in Figure 4. Reaction temperature increases biomass conversion by increasing the rate of the slow reaction.
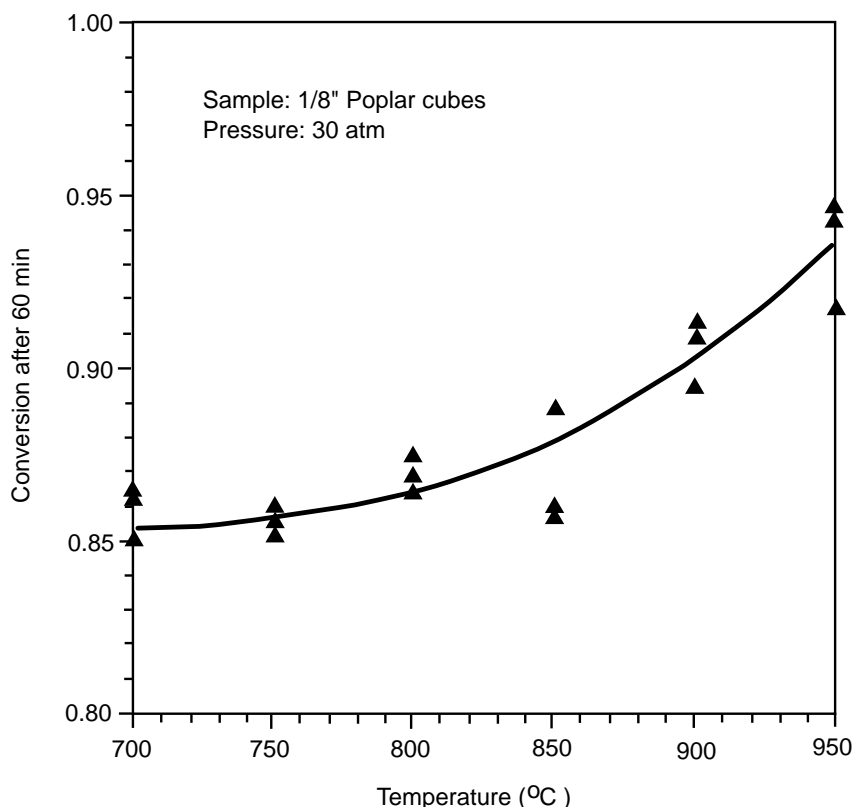

Figure 4. *Effect of reaction temperature on poplar conversion after 60 min*

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The activation energies for the rapid and slow reactions were estimated from the temperature dependencies of their initial reaction rates. The activation energies determined from the Arrhenius plots are 2.8 kcal/mol (11.7 kJ/mol) for the rapid reaction and 33.4 kcal/mol (140 kJ/mol) for the slow reaction. Very low activation energy of the rapid reaction implies that the overall reaction rates observed were restricted by either the heat transfer or the intraparticle diffusion. Since an initial temperature drop was always observed in the TBR testing, it is suggested that the heat transfer rate is slower than diffusion rate during the rapid reaction stage. Therefore, in the TBR the thermal decomposition rate is dominated by heat transfer.

Effects of Feed Gas Composition

The effect of feed gas composition was investigated by varying the flow rates of individual gas components under constant system pressure. Helium was used as an inert "makeup" gas for this purpose. The 60-min gasification tests of 1/8-in poplar particles at 30 atm and 800°C showed that conversion under pure helium is about 6% lower than that under pure hydrogen.

The gasification conversion was proportional to the partial pressures of hydrogen and steam in the feed gas as shown in Figures 5 and 6. The hydrogen in the feed gas increases biomass conversion by promoting both the rapid and slow re-

actions, while the steam in the feed gas mostly affects the rapid reaction.

Within the range of experimental conditions used, compositional changes in CH_4, CO, and CO_2 in the feed gas showed negligible effects on biomass conversion.

Effects of Catalysts

The catalytic effects of potassium carbonate (K_2CO_3) on poplar wood gasification were investigated. Catalyst was deposited on the poplar samples by evaporation from solution at 105°C. The gasification experiments were conducted with
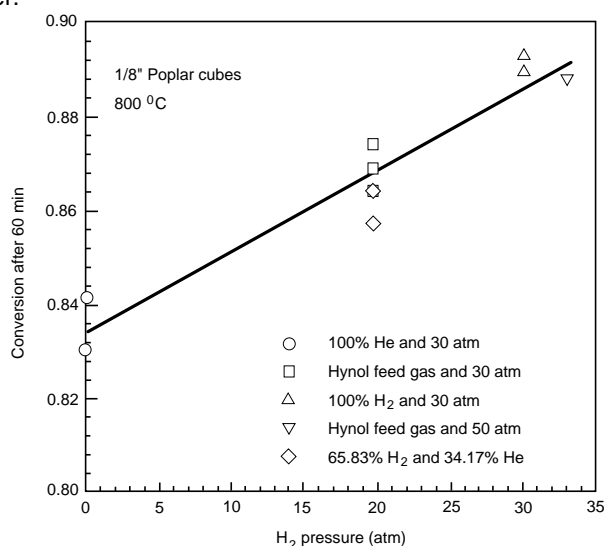

Figure 5. Effect of hydrogen partial pressure on conversion after 60 min
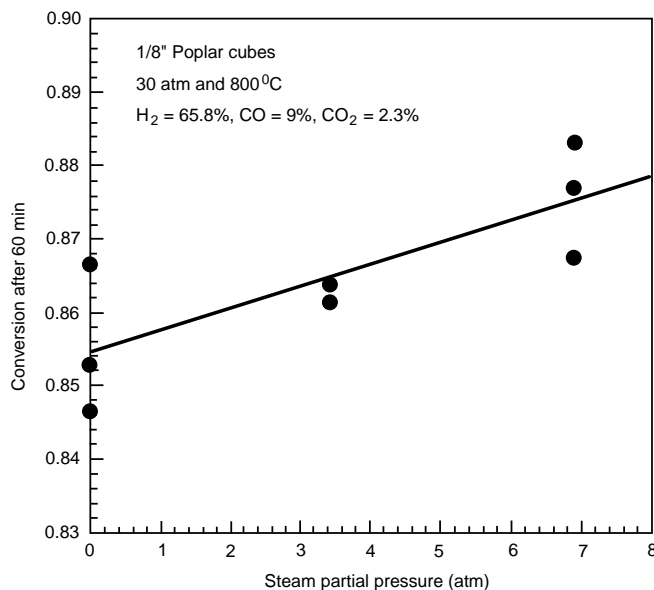

Figure 6. Effect of steam concentration on poplar wood conversion after 60 min

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both 1/8-in. poplar particles and sawdust at 30 atm and 800°C for 60 min. The experimental results were interpreted in Figure 7 where the carbon conversion data were calculated based on the actual carbon loss in the sample analyzed after gasification. Statistical calculations were conducted using student's *t* to determine the catalytic effects on carbon conversion. It was found that, with a 95% confidence level, the minimum increases in carbon conversion by K_2CO_3 were 4.5% for 1/8-in. poplar particles, and 4.2% for sawdust. The charred samples after gasification with K_2CO_3 catalyst were soft, and no agglomeration was observed during gasification.

Reactivity of Pressed Switchgrass

The gasification at 30 atm and 800°C for 60 min showed that 81-82% of pressed switchgrass could be converted into a gas product approximately equivalent to a carbon conversion of 62%. Under the same gasification conditions, the biomass conversion for 1/8-in. poplar particles is 87%. The reasons for lower conversion obtained with pressed switchgrass are not clear and need further study.
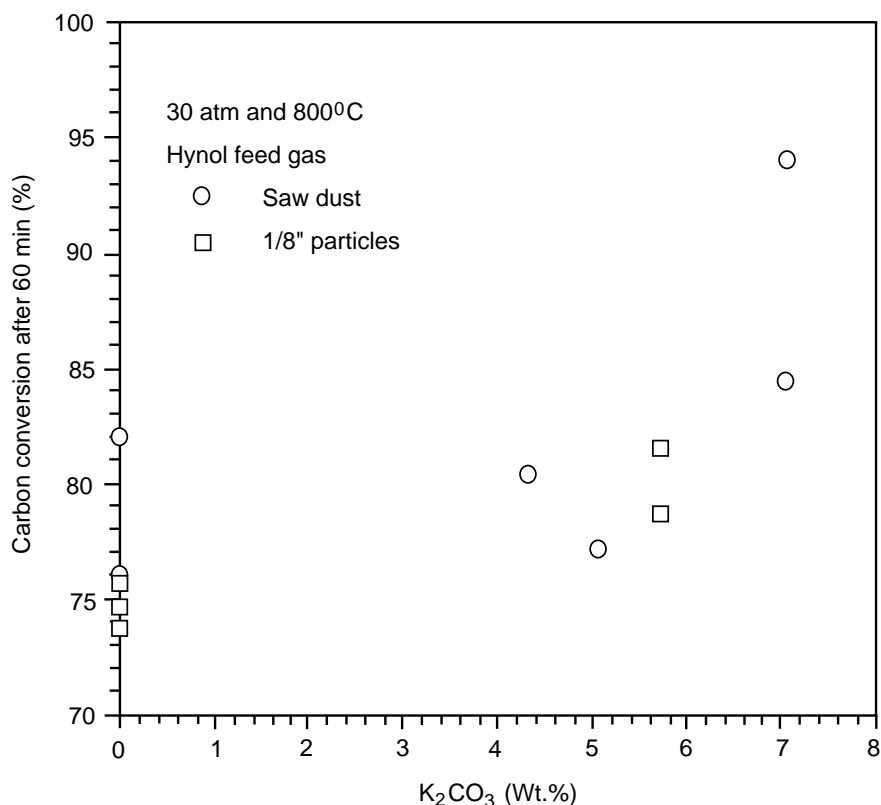

Figure 7. Effect of K_2CO_3 catalyst on carbon conversion of poplar hydrogasification

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