

UC Riverside

Recent Work

Title

Computational Modeling of Combined Steam Pyrolysis and Hydrogasification of Ethanol

Permalink

<https://escholarship.org/uc/item/3094g43n>

Authors

Singh, S
Park, C S
Norbeck, J N

Publication Date

2005-09-28

Computational Modeling of Combined Steam Pyrolysis and Hydro-gasification of Ethanol

Surinder P. Singh*, Chan Seung Park, Joseph M. Norbeck

College of Engineering-Center for Environmental Research and Technology

Department of Chemical and Environmental Engineering

University of California, Riverside

Tel: +1-951-781-5524 Email: surinder@cert.ucr.edu

We are utilizing transportation fuels at an alarming rate as the world is advancing into the new century. It is projected that petroleum may be completely utilized within the next fifty years. Research on finding alternative feedstocks and processes to develop liquid fuels for the global transportation system is gaining momentum. The energy group at CE-CERT is developing a novel multi-step process to convert carbonaceous matter to fuel. An integrated system is being developed to convert carbonaceous matter into liquid fuel. Hydrogasification refers to the reaction of carbon with hydrogen at high temperatures. A combination of steam and hydrogen in the hydrogasification section is used. Simulation studies have been carried out to model the pyrolysis and steam-hydrogen gasification (using a mixture of hydrogen and steam) steps to convert ethanol to methane. Ethanol was selected because of the simplicity of the system and to get an insight into the effects of different variables on the product gas composition and extent of gasification of a simple carbonaceous matter. Equilibrium models have been used to model the process. The methane that is produced in this process is fed to the steam methane reformer from which we get carbon monoxide and hydrogen that can be converted to FT fuel in a fischer tropesch reactor. The equilibrium model is based on the element potential method and the code is developed using Cantera. Process optimization is studied with varying reactor conditions such as temperature, pressure and steam/carbon ratios. A comparison between a pyrolysis/steam hydrogasification model with the experimental results from a flow reactor will be presented.

Keywords: Hydro-gasification, Pyrolysis, Simulation, Modeling, Renewable Energy

Background

The use of transportation fuels is increasing at an alarming rate in this century. The world is using 404 quadrillion BTUs of energy per year (Ref: <http://eia.doe.gov/>). Out of this most of the energy comes from the fossil fuels such as crude oil. America uses a quarter of the world's oil supply while holding a mere 3% of the global oil reserves. The renewable and the nuclear sources account for a very small percentage of energy usage. The energy usage is projected to increase to 632 quadrillion BTUs per year by the year 2025. In 2003 US imported 9.6 million barrels per day of crude oil. At this rate of increase in energy usage the crude oil is not projected to last long. Hence it is important to find an alternate source for transportation fuels that can sustain the growth in energy requirements.

The United States was self sufficient in terms of energy until the 1950s. After that the consumption started to increase at a much faster rate as compared to the production. In

2003, 27% of the energy was imported from other countries. Most of the energy comes from the petroleum. Renewable energy and nuclear energy constitute only a small percentage.

In 1970 the domestic supply of crude oil peaked at 11.7 million barrels per day. At that time the imports were only 3.2 million barrels per day. In 2003 the domestic supply was only 8.8 million barrels per day and the imports were 11.2 million barrels per day thereby surpassing the domestic production. The United States has been steadily been relying more and more on foreign energy since the 1970s. Another factor is China's burgeoning demand for oil. Last year China's imports were up by 30% as compared to the previous year. Oil dependence has considerable economic implications. Diminishing supply and increasing demand translate into higher costs. The world is expanding the use of petroleum and the alternative may be coal, wood or any other carbonaceous matter.

The total recoverable reserves of coal around the world are estimated at 1,001 billion tons, which is enough to last approximately 190 years at current consumption levels. Although coal deposits are widely distributed, 57 percent of the world's recoverable reserves are located in three countries: the United States (27 percent), Russia (17 percent), and China (13 percent). It is clear that the United States and other major consumers of petroleum are no longer rich in oil. They have, however, a wealth of coal reserves from which transportation fuel can be safely, affordably and cleanly generated. Centuries worth of coal reserves, 27% of the world's total in US alone, billions of tons a year of biomass, and further billions of tons of agricultural and municipal waste will be the best alternative source for feedstock to convert to transportation fuel. Hence a technology that can convert coal to liquid fuels is very promising. This technology can be easily modified to use any type of carbonaceous matter as a feedstock. The idea is to exploit the low cost and abundance of coal.

A technology that converts carbonaceous matter into fuel is the best alternative to overcome the petroleum competition. Other benefits include the ease of storage and safety issues. Liquid fuels also have the advantage of having high energy density. All the developed countries have huge infrastructure in place for the supply and usage of the liquid fuels. Hence producing liquid fuel is the best option.

The conversion techniques include methods such as partial oxidation and hydro-gasification of carbonaceous matter. Partial oxidation is done using air that results in the formation of product gases having a low calorific value because of dissolved nitrogen from air. If pure oxygen is used then the product gases have a medium calorific value but the cost of separating oxygen from air is high.

Motivation for Ethanol Equilibrium Modeling

Conversion of complex carbonaceous matter such as coal, wood and biomass requires a basic understanding of the reactions taking place for the steam hydrogasification. The effects of reactor operating conditions on the product gas formation are required. Steam and hydrogen have large impact on the product gas composition and the total gasification taking place. The effects of steam, hydrogen, temperature, and total pressure on the steam

hydrogasification of a carbonaceous matter can be understood by modeling a simple system such as ethanol. Its chemical composition is similar to wood, which might be one of the feedstocks for the process. The equilibrium model results were compared with the experimental results to verify the model. Equilibrium modeling for ethanol was done using Cantera that was developed at California Institute of Technology. Equilibrium modeling is done via element potential method. Reaction mechanism used for the equilibrium modeling was developed at Lawrence Livermore National Laboratory (Marinov 1999).

Description of Conversion Technology

The process developed at CE-CERT for converting carbonaceous matter to fuel consists of three steps. The first step involves steam hydrogasification of the carbonaceous matter. In this step the carbon in the feed is converted to gases such as methane, carbon monoxide and carbon dioxide with some char and ash residue also. The feed consists of a mixture of water and carbonaceous matter (coal) and hydrogen. The product gases include methane, carbon monoxide, carbon dioxide, hydrogen and steam. The methane rich gas from the hydrogasifier is fed into the steam methane reformer where it is converted to a mixture of carbon monoxide and hydrogen. The excess hydrogen can be recirculated into the hydrogasifier and the mixture of carbon monoxide and hydrogen in 2.1:1 ratio is fed into the Fischer-Tropsch reactor. Liquid fuel is obtained containing high carbon number alkanes.

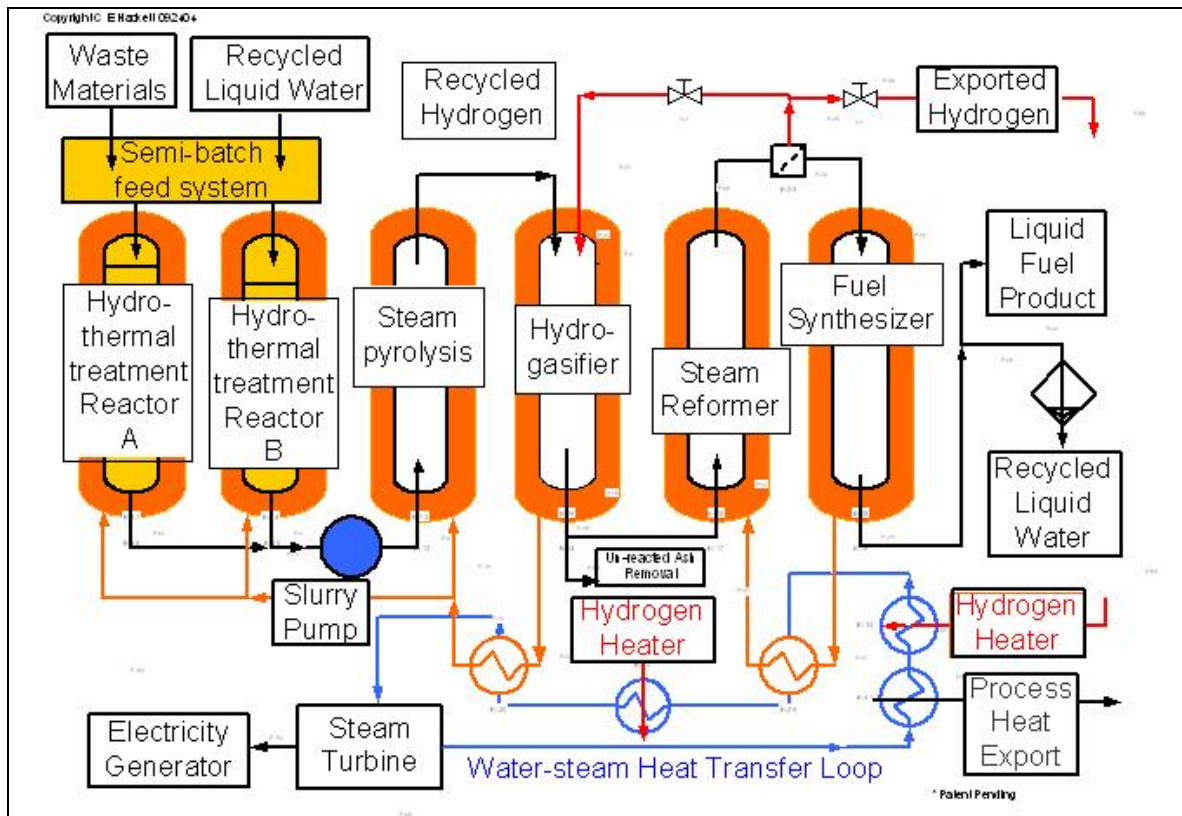


Fig. 1: Flow diagram for the complete process. Ref Hackett et al.

Steam hydrogasification is the best method in terms of cost effectiveness and also producing high calorific value gas. Steam hydrogasification is more energy efficient and easier to operate because it does not require expensive gas separating system. The CE-CERT process does not involve expensive drying of the feed material. It is observed that steam enhances the rate of conversion of carbon to methane and also to increase the composition of methane in the product gases and hence increase overall carbon conversion.

The process developed is self-sustainable because the hydrogen required in the hydrogasifier is received from the extra hydrogen that is produced in the steam methane reformer. Fischer-Tropsch reactor need H₂/CO ratio of 2.1 whereas we are producing H₂/CO ratio of 3 in the steam methane reformer. The process is also self-sustainable in terms of energy because the steam hydrogasification and Fischer-Tropsch reactions are exothermic. The energy required for the steam methane reformer is provided by the exothermic steam hydrogasification and Fischer-Tropsch reaction.

Ethanol Equilibrium Modeling

Simulation models have been developed for the processes involved in converting ethanol to methane by steam-hydrogasification. Ethanol was selected as a starting material for the modeling and simulations because of the homogeneous reaction conditions. The reaction with ethanol does not involve multiple phase reactions. Ethanol also has a chemical composition similar to wood. At later stages wood alone or as a mixture with coal can be used for the gasification hence ethanol is the ideal compound to carry out the equilibrium modeling. Models were developed to simulate the reactions taking place and the product formation under various conditions and to find out the optimum operating conditions for the hydrogasifier to maximize the formation of methane from steam hydrogasification section. Experiments were also carried out to test the validity of the models proposed. Equilibrium models have been developed using software developed at California Institute of Technology called Cantera, by element potential method. The model is used to study the product compositions under different operating conditions and different feed steam to carbon ratios.

Cantera is a very flexible tool for carrying out modeling and simulations. It is better as compared to other commercial packages used for simulations. It has the advantage of carrying out simulations and getting an insight into the various processes that are being involved while the reactions takes place. The commercial packages are not a good scientific tool because the major processes take place in the background and do not provide an insight to the basic theoretical understanding of the processes. Personal reaction mechanisms can be fed into Cantera to carry out simulations for reactions specific to our own process. Reactor networks can be defined according to our needs.

A chemical reaction mechanism developed by Marinov for high temperature ethanol oxidation was used to model the ethanol steam hydrogasification in this study. The compiled mechanism consists of 56 species and 351 reversible reactions. The product gases were optimized to produce maximum methane using the equilibrium model. Sensitivity analysis with respect to temperature, pressure and steam/carbon ratio and

hydrogen/carbon ratio was done. The model developed was based on element potential method. The equilibrium conversion of the ethanol with hydrogen and steam was calculated for temperature range of 100⁰C to 900⁰C and a pressure range of 24 bar to 34.5 bar. The hydrogen to carbon molar ratio was also varied from 0.3 to 3.0 and ethanol to water mass ratio was tested for 1:1 and 3:1 conditions.

Results and Discussion

The results indicate hydrogen to carbon ratio has a large effect on the carbon conversion efficiency to methane. When H₂/C ratio was varied from 0.3 to 3.0 the carbon converted to methane increased from 66% to 95% shown in Fig 4. This shows that increase in hydrogen composition in the feed increases the formation of methane. With increase in temperature carbon conversion to carbon monoxide starts increasing which implies that the oxidation reaction of carbon/gases increases with temperature. Methane composition decreases with increase in temperature. Pressure does not have a big impact on the carbon converted to methane, carbon monoxide and carbon dioxide in the pressure range 24-34 bar. It was observed that pressure dependence is more important when the reaction is carried out at low pressure.

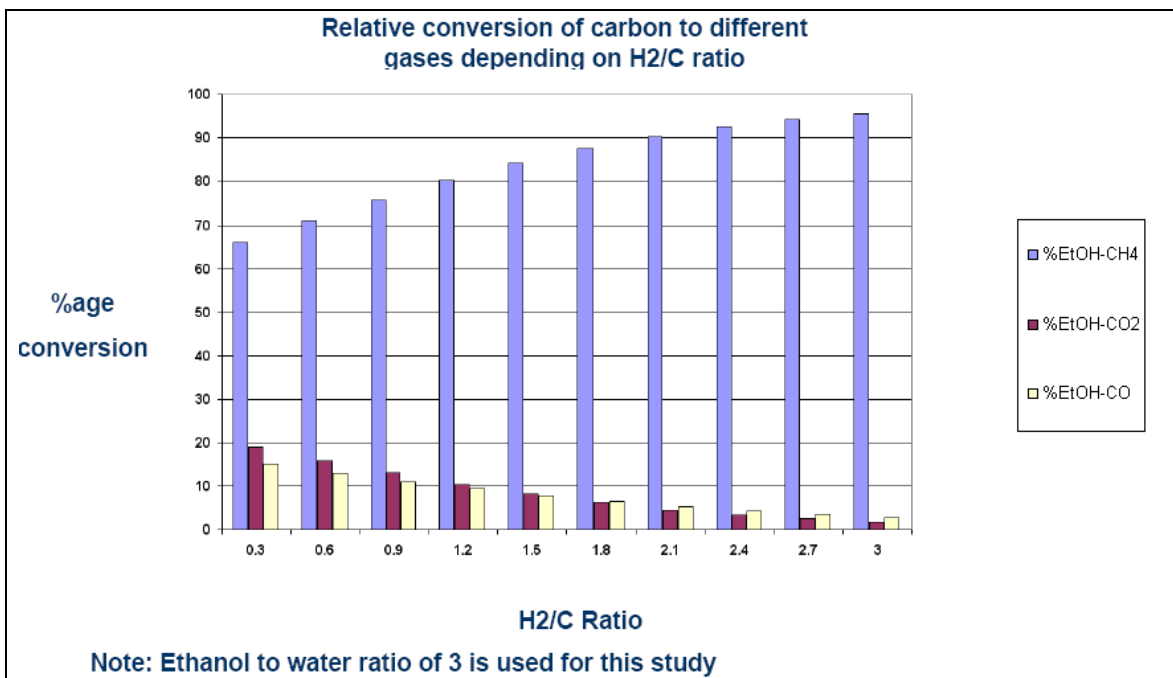


Fig. 2: Product gas dependence on hydrogen to carbon ratio for ethanol hydro-gasification (Ethanol/Water Mass Ratio=3)

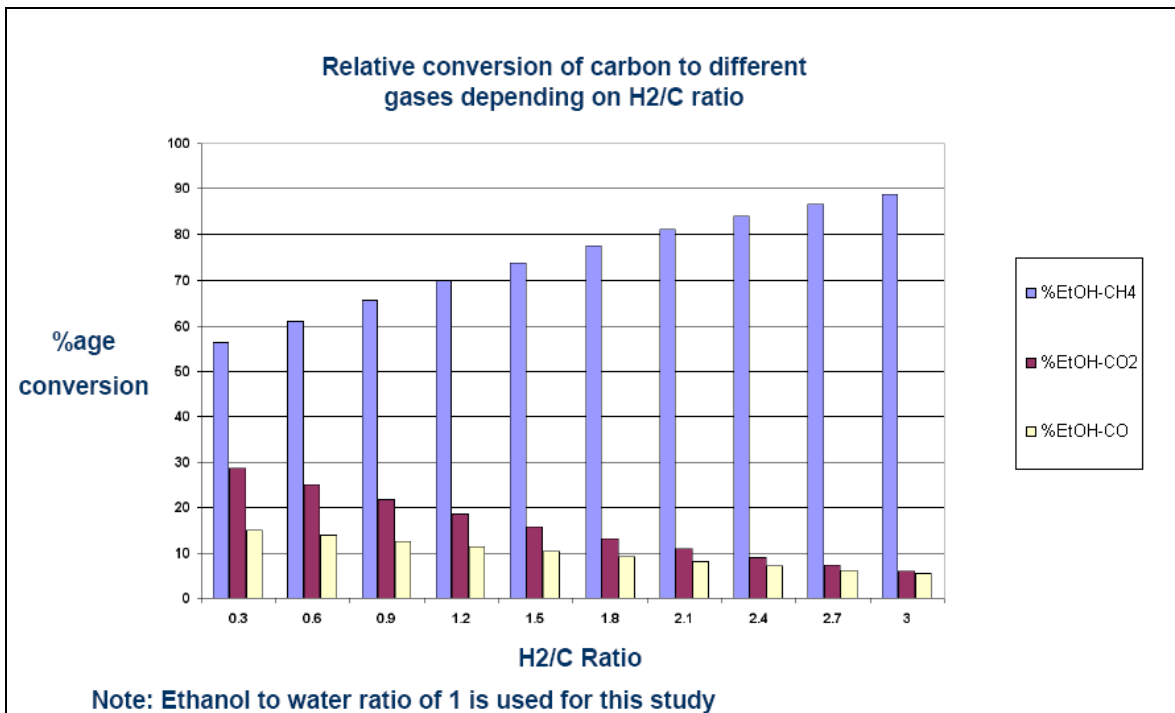


Fig. 3: Product gas dependence on hydrogen to carbon ratio for ethanol hydro-gasification (Ethanol/Water Mass Ratio=1)

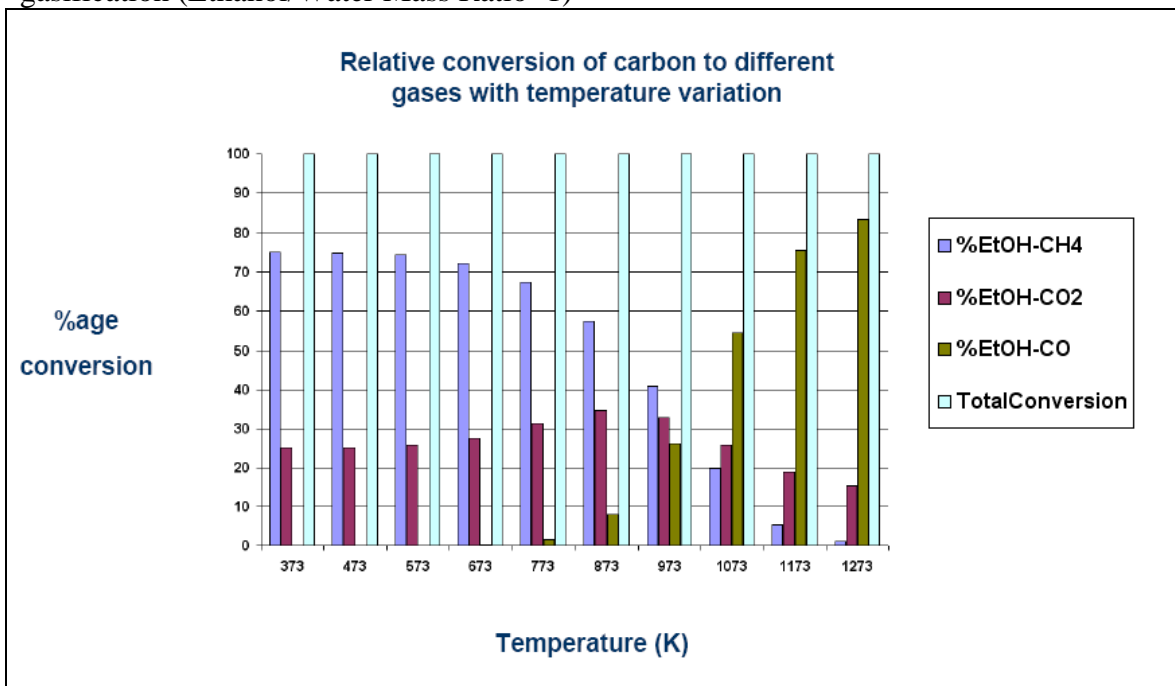


Fig. 4: Product gas dependence on temperature for ethanol gasification (without hydrogen)

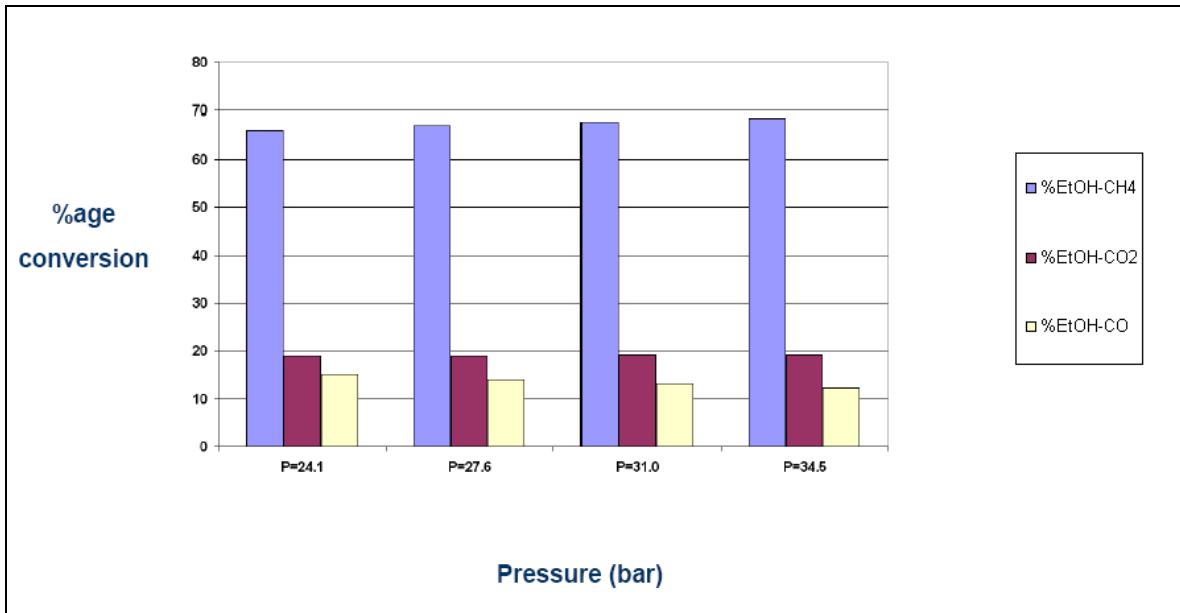


Fig. 5: Product gas dependence on pressure for ethanol hydro-gasification

Conclusions from Ethanol Equilibrium Modeling

Effect of Hydrogen/Carbon Ratio

- With increase in hydrogen/carbon ratio the percentage of carbon converted to methane increased
- With increase in hydrogen/carbon ratio the percentage of carbon converted to carbon monoxide and carbon dioxide decreased

Effect of Ethanol/Water Ratio

- With decrease in ethanol/water ratio the percentage of carbon converted to methane decreased
- With decrease in ethanol/water ratio the percentage of carbon converted to carbon dioxide increased

Effect of Temperature

- With increase in temperature the carbon converted to methane decreased. It was observed that if ethanol steam hydrogasification is done for maximum methane production then the reactor should not be operated more than 500 °C
- With increase in temperature carbon converted to carbon monoxide increased

Effect of Pressure

- Pressure has a negligible effect on the carbon conversion to gases at high pressure range

Comparison between experiments and model results

With the insight obtained from the ethanol equilibrium modeling it was desired to test it with the experimental results in a flow reactor. It is to be noted that the flow reactor was heated along its length and even though it was desired to keep a constant temperature throughout the length of the reactor some experimental difficulties did not allow the

reactor to be at constant temperature along its length. From experimental temperature observation done at the six zones it was found that the temperature increased along the length of the reactor. Equilibrium model results were obtained by using a reaction temperature that was observed in the zone six of the reactor.

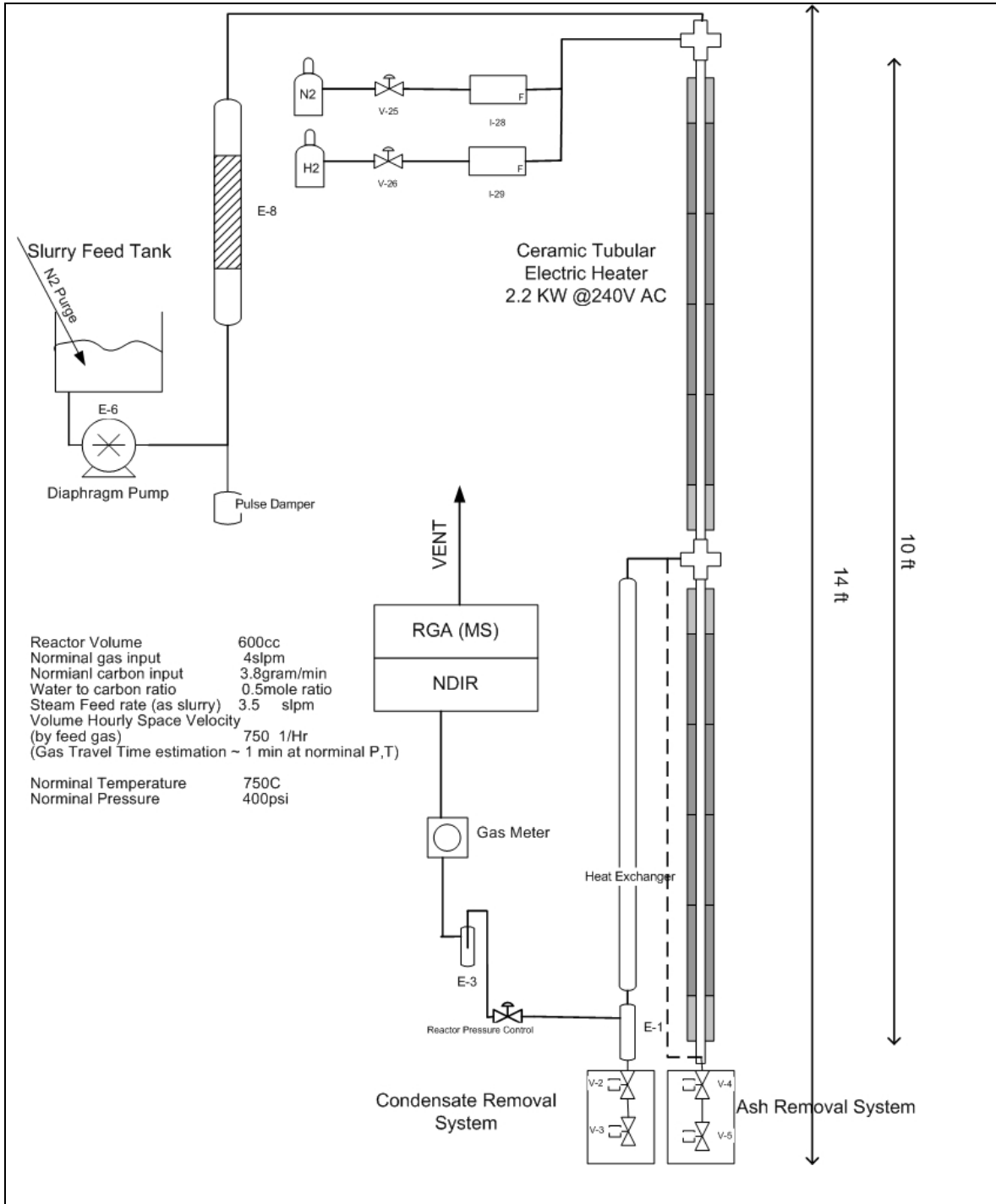


Fig 6: Free-fall reactor at CE-CERT used for steam-hydrogasification

Apparatus

The reactor used for steam hydrogasification of ethanol is shown in Fig . 6. It is a flow reactor placed vertically. The carbonaceous matter (ethanol in this case) is fed from the top along with water and gases such as hydrogen (helium in case inert gas is required) from the top. The reactor is heated along its length and temperature is monitored at six zones with the first zone at the top and the last zone at the bottom of the reactor. The product gases are obtained at the bottom of the reactor and sent to the RGA for real time analysis.

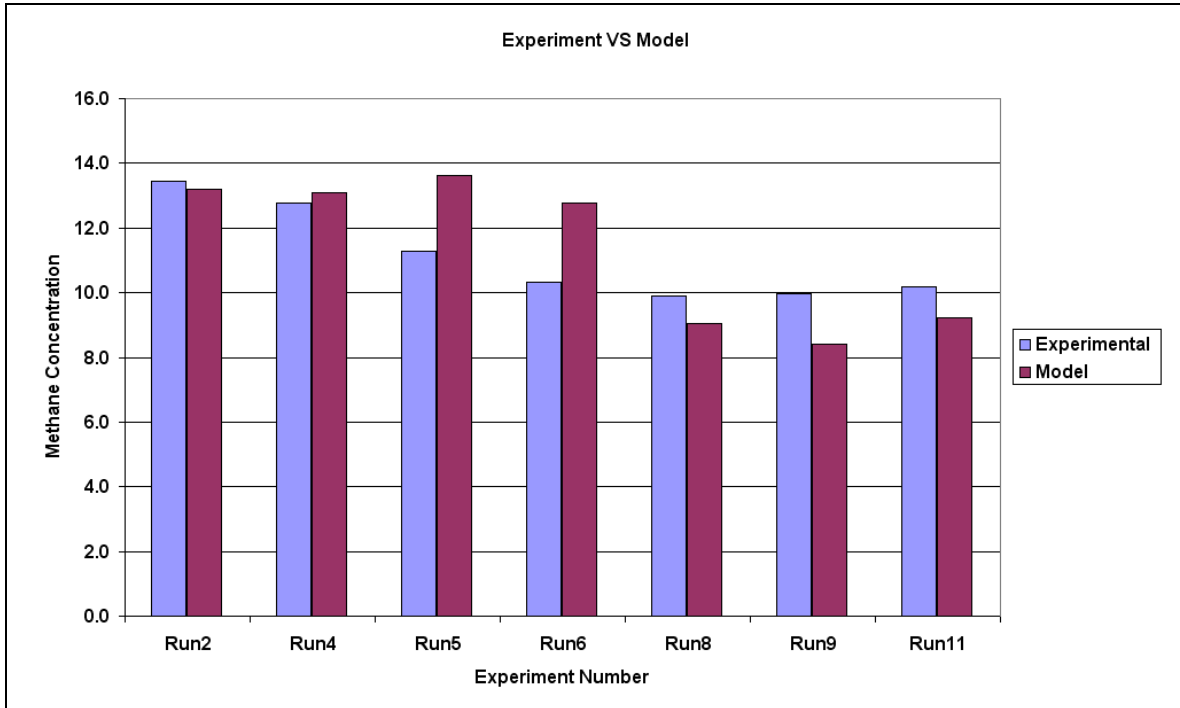


Fig. 7: Comparison of model results with experimental results for methane concentration in the free-fall reactor

The Fig. 7 shows the comparison of experimental results with the equilibrium model results for the concentration of methane at the exit of the reactor. It was assumed in the model calculations that the exit gases from the flow reactor had reached equilibrium at the exit temperature in the zone six. The experimental results were found to be in excellent agreement with the model results. The difference between the results increased in the experiments where it was observed that the average temperature was significantly different then the zone six temperature. It was previously shown that the temperature had a large impact on the equilibrium modeling and hence the differences are justified.

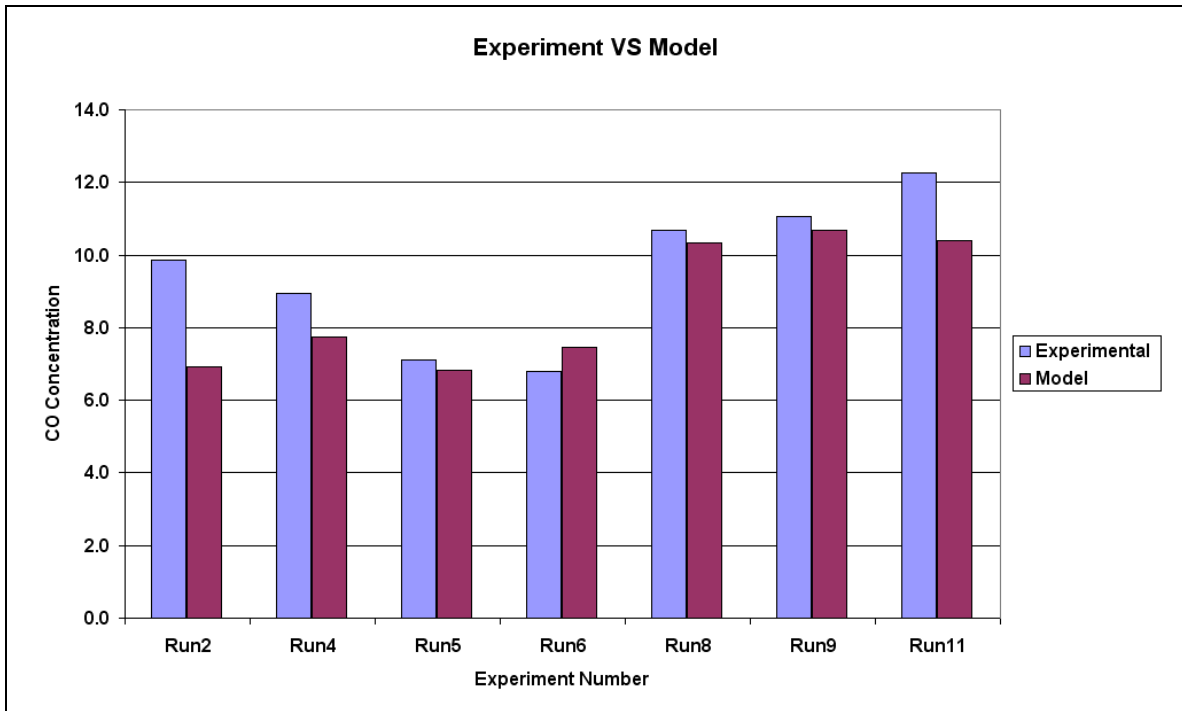


Fig. 8: Comparison of model results with experimental results for CO concentration in the free-fall reactor

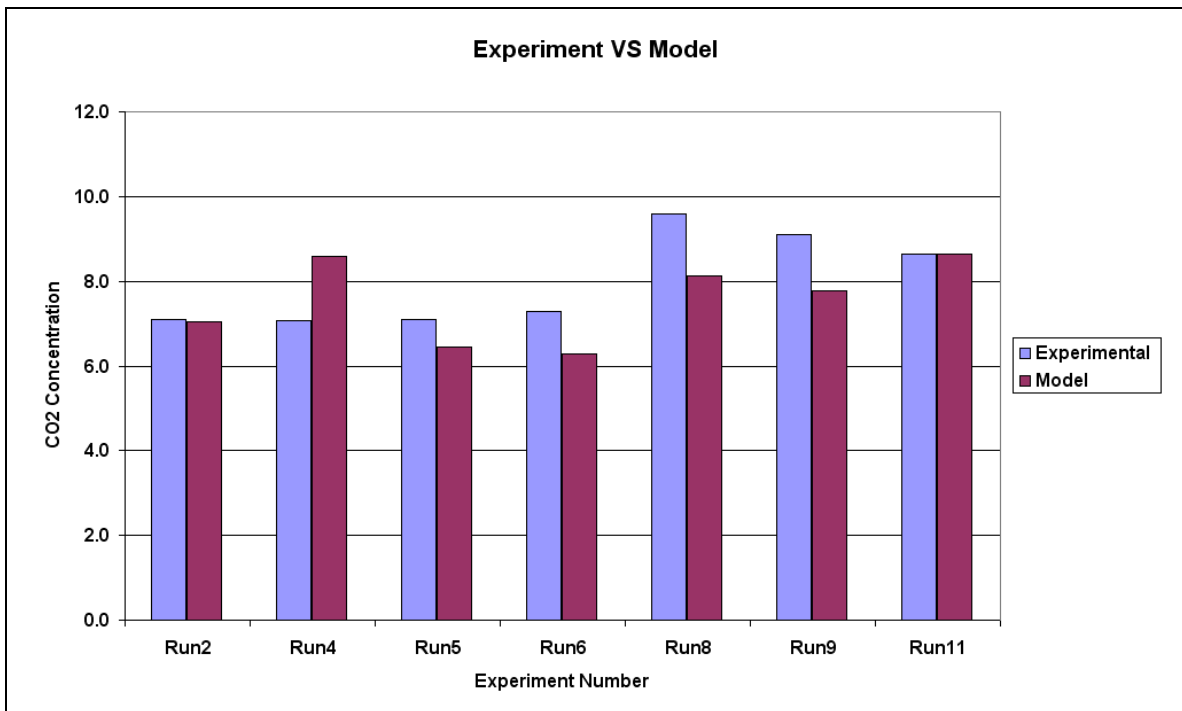


Fig. 9: Comparison of model results with experimental results for CO₂ concentration in the free-fall reactor

Conclusions

The ethanol equilibrium modeling showed that temperature had large influence on the product gas composition from the gasification of ethanol. Pressure was found to have negligible influence on the product gases. Steam and hydrogen had considerable influence on the product gas composition. The comparison of the model results with the experimental results from a flow reactor were in excellent agreement even though the model assumed that the product gases were under equilibrium conditions at the exit of the reactor. The effects of these variables on ethanol gasification gives an insight into the product gas formation which will be helpful in determining the operating conditions for the steam hydrogasification of complex carbonaceous matter such as coal and wood or their mixtures.

References

1. Agarwal, AK. (1980). The coal char reaction with CO₂-CO gas-mixtures. *Industrial & engineering chemistry process design and development*, 19(3), 364-371.
2. *Alternative Fuels*, Lee, S., Applied Energy Technology Series, Taylor and Francis (1996)
3. Anthony, DB (1976). Rapid devolatilization and hydrogasification of bituminous coal. *Fuel*, 55(2), 121-128.
4. *Biomass Gasification Principles and Technology*, Reed, T.B. (ed.), Noyes Data Corporation (1981)
5. *Chemistry of coal utilization*, Elliot, M.A. (ed.), Second supplementary volume, 688-778 (1981)
6. *Chemistry of coal conversion*, Schlosberg, R.H. (ed.), Plenum Press, New York (1985)
7. Donskoi, E. (1999). Approximate modelling of coal pyrolysis. *Fuel*, 78(7), 825-835.
8. Gonzalez, JF. (2002). Hydrogasification of almond shell chars. Influence of operating variables and kinetic study. *Industrial & engineering chemistry research*, 41(15), 3557-3565.
9. Gonzalez, JF. (2003). Pyrolysis of cherry stones: energy uses of the different fractions and kinetic study. *Journal of analytical and applied pyrolysis*, 67(1), 165-190.
10. <http://www-cms.llnl.gov/combustion/combustion2.html>
11. Johnson JL, *Kinetics of Coal Gasification*, New York, John Wiley & Sons, (1979)
12. Juntgen, H. (1981). Reactivities of carbon to steam and hydrogen and applications to technical gasification processes- A review. *Carbon*, 19(3), 167-173.
13. Mann, MD. (2004). Modeling reaction kinetics of steam gasification for a transport gasifier. *Fuel*, 83(11-12), 1643-1650.
14. Marinov, N. M, "A Detailed Chemical Kinetic Model for High Temperature Ethanol Oxidation" *Int. J. Chem. Kinet.* 31:183-220 (1999); Lawrence Livermore National Laboratory, Livermore, CA, UCRL-JC-131657.
15. Matsuoka, K. (2003). High-pressure coal pyrolysis in a drop tube furnace. *Energy & fuels*, 17(4), 984-990.
16. Molina, A. (1998). Reactivity of coal gasification with steam and CO₂. *Fuel*, 77(15), 1831-1839.

17. Muhlen, HJ. (1985). Kinetic-studies of steam gasification of char in the presence of H₂, CO₂ and CO. *Fuel*, 64(7), 944-949.
18. Porada, S. (2004). The influence of elevated pressure on the kinetics of evolution of selected gaseous products during coal pyrolysis. *Fuel*, 83(7-8), 1071-1078.
19. Rai, C. (1979). Kinetic-models for pyrolysis and hydrogasification of hanna coal. *Fuel*, 58(8), 603-608.
20. Schimal, M. (1982). Kinetics of coal gasification. *Industrial & engineering chemistry process design and development*, 21(2), 256-266.
21. Ulloa, C. (2004). Distribution of activation energy model applied to the rapid pyrolysis of coal blends. *Journal of analytical and applied pyrolysis*, 71(2), 465-483.
22. Xu, WC. (2003). High pressure hydrolyrolysis of coals by using a continuous free-fall reactor. *Fuel*, 82(6), 677-685.