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Co-gasification of wood and polyethylene with the aim of CO and H₂ production

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Abstract This article describes the gasification of polyethylene–wood mixtures to form syngas (H₂ and CO) with the aim of feedstock recycling via direct fermentation of syngas to ethanol. The aim was to determine the effects of four process parameters on process properties that give insight into the efficiency of gasification in general, and particularly into the optimum gasification conditions for the production of ethanol by fermentation of producer gas. Gasification experiments (fluidized bed, 800°–950°C) were done under different conditions to optimize the composition of syngas suitable for fermentation purposes. The data obtained were used for statistical analysis and modeling. In this way, the effect of each parameter on the process properties was determined and the model was used to predict the optimum gasification conditions. The parameters varied during the experiment were gasification temperature, equivalence ratio, the ratio of plastic to wood in the feed, and the amount of steam added to the process. The response models obtained proved to be statistically significant in the experimental domain. The optimum gasification conditions for maximization of carbon monoxide and hydrogen production were identified. The conditions are: temperature 900°C, equivalence ratio 0.15, amount of plastic in the feed 0.11 g/g feed, and amount of steam added 0.42 g/g feed. These optimum conditions are at the edge of the present experimental domain. The maximum combined CO and H₂ efficiency was 42%, and for the maximum yield of CO and H₂ it is necessary to minimize the polyethylene content, minimize the added steam and the equivalence ratio, and maximize temperature.

Key words Gasification · Wood · Waste plastics · Modeling · Polyethylene · CO · H₂-production

Introduction

Developing countries are dealing with severe sustainability issues, especially concerning energy needs and waste handling. Over the past decades, the use of plastics has become increasingly common in developing countries; methods to dispose of plastic waste, however, have not developed significantly in these countries. Plastic waste is usually dumped together with organic waste. With the increasing need for energy, the increasing dependency on fossil fuels, and the growing depletion of petroleum reserves, the call for more sustainable solutions becomes louder.

The co-gasification of plastic waste and biomass and the subsequent fermentation of the syngas formed to ethanol may be a contribution to the solution of the aforementioned problems. The plastic waste is processed, biomass is used in a more efficient way, and a fuel for transport is produced. It is also a step toward a more sustainable solution to fuel and waste problems, because the conversion of waste to ethanol will reduce the use of fossil fuels and thus save fossil resources at the same time.

Gasification is a very old technology; it was used over 180 years ago in blast furnaces in the iron industry. Soon after that, producer gas was used for heating, lighting, and power generation.¹ Gasification is a method for converting carbonaceous material to gas. This gas can be used for combustion or for the production of chemicals, for example solvents. In recent decades, much research has been done on the gasification of biomass for the production of renewable energy and fuels. Pinto et al.² studied the combined steam gasification of biomass and plastic. They studied the effect of the plastic content, the effect of the amount of steam, and the effect of the temperature on the final gas composition.

The production of ethanol by fermentation of sugars is a very old process. Humans have been preparing fermented beverages for more than 5000 years. Fermentation of gasification product gases, however, is a rather new development. Datar et al.³ are working on the fermentation of syngas, and have successfully produced ethanol.

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The gasification/fermentation pathway is a very interesting development. In traditional fermentation processes, lignin, an important component of biomass, and plastics cannot be fermented. Gasification and subsequent fermentation of the produced gas enables fermentation of any carbon and hydrogen-containing material. The resulting fuel-grade ethanol should make economical operation possible in the near future.

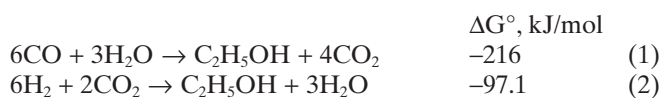
Theory

The fermentation of biomass is a very old process. Sugars have been fermented to ethanol for millennia; the fermenting of syngas however is rather new. Fermentation reactions are biological processes. A disadvantage of these processes is that they are generally slower than catalytic processes. There are, however, several advantages in comparison with catalytic processes, for example:^{4,5}

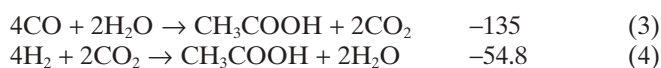
- Higher specificity
- Higher yields
- Lower energy costs
- Possible higher resistance to poisoning

Datar and others^{3,6} have reported the successful fermentation of syngas to ethanol. Fermentation by the acetogens used in that study is reported to follow the acetyl-CoA pathway. Fermentation tests have been carried out in various reactor types. Phillips et al.⁶ used a stirred batch reactor. Klasson et al.⁷ used several continuous reactors, namely a stirred-tank reactor, a packed bubble column, and a trickle-bed reactor. The processes took place at 37°C and the pH was controlled. A frequently used bacterium is *Clostridium ljungdahlii*. This bacterium produces acetic acid as a by-product.

The overall reactions that form ethanol from CO, CO₂, and H₂ are:



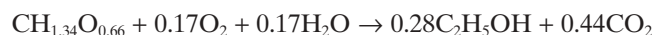
Competitive reactions form acetic acid as follows:



Via reaction (1), CO is converted to ethanol, producing CO₂. H₂ is needed to convert the produced CO₂ to ethanol by way of reaction (2). It follows that the maximum ethanol yield depends on the composition of the syngas. From the above reactions, it is clear that CO, H₂, and CO₂ are the only useful gases for the fermentation process.

Reactions (3) and (4) produce acetic acid. There is competition between ethanol and acetic acid formation, and the ratio of ethanol and acetic acid produced can be influenced by several parameters. Klasson et al.⁷ managed to produce ethanol and acetic acid with a molar product ratio of 4:1.

To couple both processes (gasification and fermentation) it is crucial that as much CO and/or H₂ as possible can be retrieved from the biomass/waste input streams. Especially with the use of polyethylene (PE), ethylene will be formed, which is detrimental to the fermentation bacteria.⁵ As a result, it is better to choose process conditions that minimize ethylene production and maximize CO and H₂ production. The ratio of CO to H₂ is not critical because both components react to form the same amount of ethanol. This means that the C/H ratio of the feed to the gasifier is not crucial as long as the C and H are converted to CO/H₂ mixtures. In the ideal case, this would lead to the following reaction for pure wood:



$$\Delta H^\circ = -59 \text{ kJ/mole}$$

Because the fermentation produces CO₂, there is always enough CO₂ for reaction (2). In this work, the influence on the CO and H₂ yield of feed composition (wood mixed with polyethylene), the amount of steam, the equivalence ratio (ER), and the temperature was studied. The aim was to determine the optimal conditions for maximizing the CO yield, the H₂ yield, and their combination. The wood-polyethylene mixture was chosen as a model component because wood represents biomass and polyethylene is known to be the major plastic component in household waste.

Experimental methods

The gasification experiments were carried out in fluidized bed gasifier equipment described elsewhere.^{8,9} Porous γ -alumina powder was used as bed material with a bed height of 10 cm. The average particle diameter of the powder was 98 μm , the same as that used by Slapak.¹⁰ The observed minimal fluidization velocity at ambient temperature with pure nitrogen as a carrier gas was found to be 0.27 cm/s.

The operating conditions studied were: the temperatures tested were 770°C until 950°C; the feedstock composition used was a wood:polyethylene ratio of 0–0.4 on a weight basis (g PE/g feed mixture); the amount of steam was varied between 0.4 and 1.4 g steam/g feed mixture (the optimum range as reported by Franco et al.¹¹); and the ER was varied between 0.1 and 0.4.

From elemental analysis of wood fuel and PE and considering the major elements, the wood fuel and PE may be represented on a molar basis as CH_{1.34}O_{0.66} Dry Ash Free (DAF) and C₂H₄, respectively. Based on this composition, the ER was calculated; complete combustion to CO₂ and H₂O being an ER of 1 (mole/mole). The nitrogen flow rate was adjusted to keep the total flow of gas within 1–2 l/min (room temperature) to maintain the experiments in the same fluidizing regime.

The effects of ER, process temperature, feedstock composition, and steam addition on total CO and H₂ efficiency was determined. The CO and H₂ efficiency was defined as:

Table 1. Gas compositions of the gasification experiments

| Trial | Conditions | | | | Results | | | | | | |
|-------|--------------------------|------------------------|--------|--------|--|------|------|------|-----|------|------------------------|
| | PE content (Wt fraction) | Steam/feed ratio (w/w) | ER (-) | T (°C) | Gas composition excluding nitrogen (v/v) (%) | | | | | | Total gas flow (l/min) |
| 1 | 0.11 | 0.43 | 0.17 | 800 | 27.5 | 27.2 | 27.2 | 10.9 | 5.6 | 1.5 | 1.3 |
| 2 | 0.32 | 0.42 | 0.14 | 800 | 23.0 | 26.1 | 26.9 | 13.4 | 7.8 | 2.8 | 1.6 |
| 3 | 0.11 | 0.43 | 0.17 | 900 | 25.7 | 30.8 | 26.5 | 11.8 | 4.6 | 0.5 | 1.7 |
| 4 | 0.32 | 0.42 | 0.14 | 900 | 22.6 | 32.1 | 23.0 | 15.3 | 6.4 | 0.7 | 2.0 |
| 5 | 0.11 | 0.43 | 0.50 | 800 | 20.4 | 15.9 | 43.5 | 8.6 | 4.3 | 7.4 | 1.5 |
| 6 | 0.32 | 0.42 | 0.42 | 800 | 16.3 | 15.3 | 40.6 | 11.2 | 8.2 | 8.4 | 1.8 |
| 7 | 0.11 | 0.43 | 0.50 | 900 | 21.6 | 17.0 | 34.9 | 11.1 | 3.7 | 11.8 | 1.7 |
| 8 | 0.32 | 0.42 | 0.42 | 900 | 19.0 | 19.0 | 33.7 | 14.7 | 5.4 | 8.3 | 1.9 |
| 9 | 0.11 | 1.30 | 0.17 | 800 | 19.2 | 37.0 | 31.0 | 8.2 | 2.7 | 1.9 | 2.0 |
| 10 | 0.32 | 1.27 | 0.14 | 800 | 18.1 | 28.9 | 28.2 | 14.0 | 8.2 | 2.6 | 1.7 |
| 11 | 0.11 | 1.30 | 0.17 | 900 | 22.4 | 33.0 | 29.1 | 11.4 | 3.6 | 0.6 | 2.0 |
| 12 | 0.32 | 1.27 | 0.14 | 900 | 19.9 | 27.6 | 25.9 | 18.0 | 7.6 | 0.9 | 1.9 |
| 13 | 0.11 | 1.28 | 0.50 | 800 | 19.0 | 17.8 | 42.4 | 9.1 | 3.8 | 7.9 | 1.8 |
| 14 | 0.33 | 1.28 | 0.42 | 800 | 15.6 | 18.9 | 36.9 | 11.7 | 6.9 | 10.0 | 2.1 |
| 15 | 0.11 | 1.28 | 0.50 | 900 | 18.2 | 19.7 | 36.4 | 10.4 | 3.5 | 11.8 | 2.0 |
| 16 | 0.33 | 1.28 | 0.42 | 900 | 12.8 | 23.8 | 32.2 | 14.2 | 5.5 | 11.5 | 2.2 |
| 17 | 0.00 | 0.88 | 0.38 | 850 | 26.7 | 19.1 | 40.9 | 9.3 | 3.0 | 0.9 | 1.5 |
| 19 | 0.22 | 0.85 | 0.30 | 800 | 18.6 | 21.9 | 40.0 | 11.0 | 6.2 | 2.4 | 1.8 |
| 21 | 0.21 | 0.85 | 0.00 | 850 | 23.9 | 40.5 | 14.9 | 11.6 | 7.5 | 1.7 | 1.7 |
| 23 | 0.22 | 0.00 | 0.31 | 850 | 25.9 | 17.8 | 35.3 | 13.1 | 7.2 | 0.6 | 1.6 |
| 25 | 0.22 | 0.86 | 0.31 | 850 | 19.2 | 21.1 | 36.0 | 14.1 | 6.7 | 2.9 | 1.6 |
| 26 | 0.22 | 0.86 | 0.31 | 850 | 19.7 | 19.9 | 36.1 | 14.0 | 7.2 | 3.1 | 1.6 |
| 27 | 0.22 | 0.85 | 0.30 | 850 | 20.0 | 21.3 | 34.7 | 14.3 | 6.6 | 3.2 | 1.8 |
| 28 | 0.22 | 0.86 | 0.31 | 850 | 20.7 | 19.9 | 35.8 | 13.9 | 6.6 | 3.1 | 1.7 |

PE, polyethylene; ER, equivalence ratio; T, temperature

^aOther compounds are C₂H₆, C₃H₈, C₃H₆, and C₄H₁₀

$$CO\text{ and }H_2\text{ efficiency} = \frac{\left(\frac{(f_{CO} + f_H) \times F}{V_M} \right)}{\left(\frac{r_H}{n_{H_2}^H} + r_C \right)} \times 100\% \quad (5)$$

Where r_H is the rate of hydrogen feed in moles of elemental H/min, $n_{H_2}^H$ is the number of H atoms in one H₂ molecule (i.e., 2), r_C is the rate of carbon feed in moles of elemental C/min, F is the total gas flow rate (l/min), f_{CO} is the volume fraction of CO in the gas phase, f_H is the volume fraction of H₂ in gas phase, and V_M is the molar volume of gas at 298 K (i.e., 24.4 l/mol gas).

Results and discussion

Table 1 shows the syngas composition as a function of temperature, ER, feed composition, and steam addition. These data were modeled with the aid of the computer program MODDE (Umetrics AB, Malmö, Sweden), leading to the following statistical formula for CO and H₂ efficiency:

$$Y = \left(\begin{array}{l} C_0 + C_1 \cdot ER + C_2 \cdot T + C_3 \cdot S + C_4 \cdot P + C_5 \cdot ER^2 \\ + C_6 \cdot T^2 + C_7 \cdot S^2 + C_8 \cdot P^2 + C_9 \cdot ER \cdot T + C_{10} \cdot ER \cdot S \\ + C_{11} \cdot ER \cdot P + C_{12} \cdot P \cdot S + C_{13} \cdot T \cdot P + C_{14} \cdot S \cdot P \end{array} \right)^{C_{15}} \quad (6)$$

Table 2. Model coefficients for the statistical model of CO and H₂ efficiency in gasification experiments

| Response model coefficient | Parameter value |
|----------------------------|-----------------|
| C ₀ | -7.18381E-01 |
| C ₁ | 5.91432E-02 |
| C ₂ | 1.86047E-03 |
| C ₃ | -5.57437E-02 |
| C ₄ | 4.46713E-02 |
| C ₅ | 0.00000E+00 |
| C ₆ | -1.17419E-06 |
| C ₇ | -7.84521E-03 |
| C ₈ | 0.00000E+00 |
| C ₉ | 0.00000E+00 |
| C ₁₀ | -2.08844E-02 |
| C ₁₁ | 0.00000E+00 |
| C ₁₂ | 8.19561E-05 |
| C ₁₃ | 0.00000E+00 |
| C ₁₄ | 0.00000E+00 |
| C ₁₅ | -1.00000E+00 |

Table 2 shows the results of the statistical analysis of the coefficients for the CO and H₂ efficiency model. Figure 1 shows that the quality of the model (the accuracy of the fit to the measured data) is reasonably good. Figure 2 shows the CO and H₂ efficiency as a function of the amount of steam added to the feed and the temperature at an ER of 0.15 and a PE wt% fraction in the feed of 0.11. It can be seen immediately that the maximum amount of CO and H₂ generation occurs at high temperatures. The higher the tem-

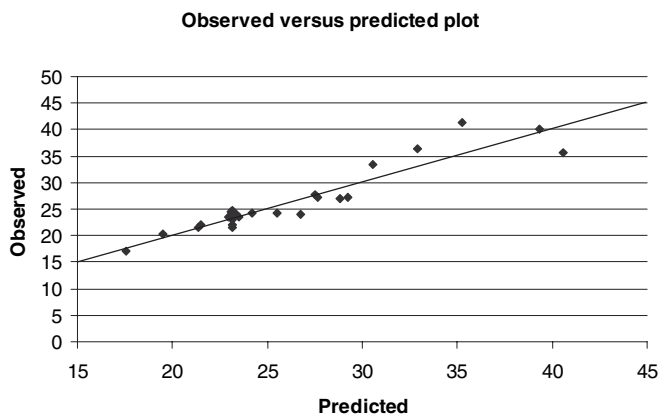


Fig. 1. Observed (symbols) versus predicted values of CO and H₂ efficiency (line)

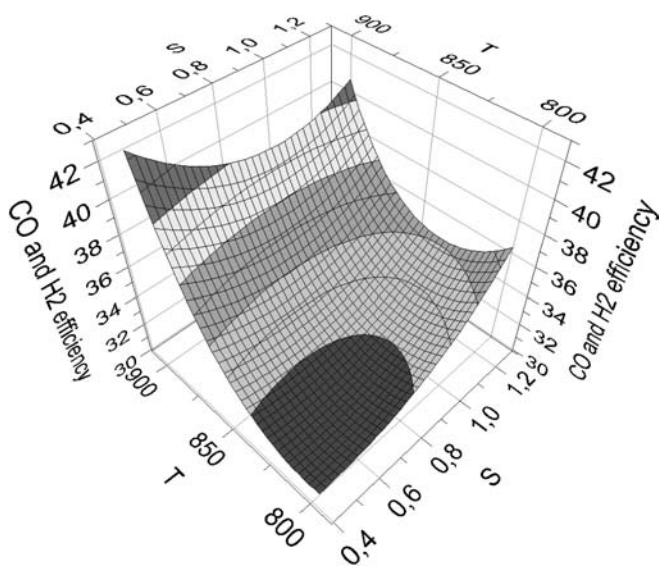


Fig. 2. CO and H₂ efficiency as a function of temperature (T) and the amount of steam added to the feed (S) at an equivalence ratio of 0.15 and a polyethylene weight fraction in the feed of 0.11

perature, the higher the amount of CO and H₂ formed. This is according to expectations as syngas formation is thermodynamically favored at high temperatures (>1000°C). The plastic fraction seems to be not favorable to the overall efficiency for the process conditions investigated as it is known (Kasteren et al., 2002) that PE gasification at 950°C leads to char formation and relatively low carbon to gas conversion (50%).¹⁰ In contrast, wood forms more CO as a function of increasing temperature.¹²

The yield of CO and H₂ is optimal at high temperatures, low PE content, and low ER. The ER should not be higher than 0.2 to prevent too much CO₂ formation. The addition of steam should either be low or high for optimal CO and H₂ efficiency. From an energetic point of view, as low an amount of steam as possible is preferable, as steam production requires energy. The optimal amount of steam is not clear because the real optimum is outside the experimental domain of our experiments.

Conclusions

The response models obtained proved to be statistically significant in the experimental domain. The optimum gasification conditions for maximal CO and H₂ production were identified as a temperature of 900°C, an ER of 0.15, a feed plastic content of 0.11 g/g feed, and steam addition at 0.42 g/g feed. These optimum conditions are at the edge of the present experimental domain. The maximum combined CO and H₂ efficiency was 42%, and for the maximum yield of CO and H₂ it is necessary to minimize the PE content, minimize the added steam and the equivalence ratio, and maximize the temperature.

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