

# Hydrogen Production from Vegetable Oil

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**ABSTRACT:** We designed a new small-scale device for CO and H<sub>2</sub> production by organic fuel reformation. The active region of the reformer consists of wall-through flow manifolds which decreases the gas speed of the fuel-air mixture at the area of reformation. This system does not use catalysts, and thus it is not sensitive to fuel impurities. Reformation of soybean oil shows a 20-30% conversion of carbon into CO, with its concentration reaching 13 % of the outgoing gas. From calculations, the expected content of hydrogen reaches about 16 % by volume.

**Keywords:** biomass reformation, synthesis gas, hydrogen production

## 1. INTRODUCTION

Biomass has great potential as a clean and renewable feedstock for producing modern energy carriers [1-5].

This paper focuses on the process of soybean oil reformation, where the resultant synthesis gas may subsequently be used for the production of electricity or fuels. The gasifier is one of the least efficient unit operations in the whole biomass-to-energy technology chain, and an analysis of gasifier efficiency alone can substantially contribute to the efficiency of the chain.

Our previous work was concerned with diesel fuel reformation for production of synthesis gas [6, 7]. The syn-gas from reformation was introduced into the engine or in the exhaust channel to react with the exhaust or to support the catalyst [8].

In this study, we produced a small scale, portable reformer without catalysts, to be less dependent on fuel impurities. Other issues regarding catalysts are the costs, as well as catalyst contaminations that lead to efficiency reductions and lifetime decreases.

## 2. EXPERIMENTAL EQUIPMENT

### 2.1 Reformer

The reformer consists of three main parts. The first one is the active element - SiC filters by Notox that have diameters of 20 and 28 mm, respectively, and a length of 103 mm. The outer cylindrical wall of the filter was coated with an electrically conductive paste, Pyro-Duct 597-C of Aremco Products Inc. The second part is a spraying nozzle - Air atomizing 1/8JJAU-SS BSPI of Spraying Systems. We sometimes made a modification to this nozzle allowing a larger amount of air to pass through. The last part is the housing, with thermal insulation, electrode feed-through, openings to fixed and movable thermocouples, opening to the pressure gauge, and opening to the oil-air mixture input. A diagram of the assembled system is shown in Figure 1.

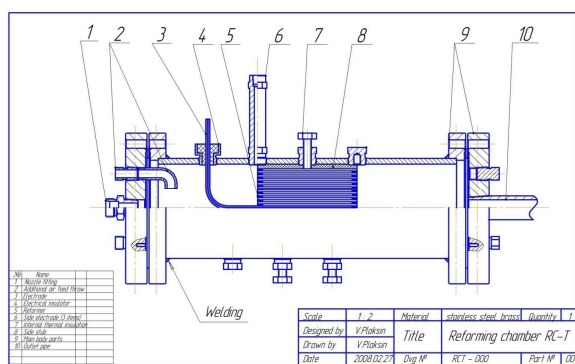


**Figure 1:** Reforming apparatus. 1. Nozzle fitting; 2. Additional air feed-through; 3. Electrode; 4. Electrical insulator; 5. Reforming element; 6. Thermocouple fitting; 7. Side electrode (3 items); 8. Internal thermal insulator; 9. Main body parts; 10. Outlet pipe.

## 2.2 Active Reforming Element

A reformer converts liquid fuel into a gaseous fuel stream containing hydrogen and carbon monoxide as major components. There are several such systems, such as catalytic partial oxidizers (CPOx), non-catalytic (homogeneous) partial oxidizers (POx), or auto thermal reformers (ATR). From the mixture of fuel, water and/or air, they generate the gas streams. For the reaction area they use chambers, pipes, pellets, powders, foams, honeycombs, or fibres. [See for example WO 2001/052978, WO 2001/024922, WO 2001/012540.] In all of these reaction elements the gas flows mostly in the axial direction. Therefore, the reformation rate is limited whether by the flame propagation velocity, or by the contact area between gas and surface. In the last case, the backpressure of the device is also a subject to consider in practical application. The efficiency of the reformer increases by turning the direction of the flame forwards, whereby increasing the effective burning surface. That was done by using the labyrinth structure of reformer.

A new structure which is not seen in conventional techniques was examined. In the device the fuel-air mixture flows through the reforming area in a way that increases the cross-sectional area far beyond

that of a conventional reformer. This increased cross sectional area increases the productivity and rate of the reforming reaction, and it is possible to decrease or eliminate the presence of catalyst.

Eliminating the catalyst is one of the goals of the work, because the catalyst raises manufacturing costs and has the problem of contamination with impurities of supplied fuels, such as sulphur.

As an active reforming element, we adopted a columnar honeycomb structural body comprising a large number of through holes placed in parallel with one another in the axial direction as shown in Figure 2. The wall portions are porous and made of SiC, a ceramic material, as in 10. of Figure 2; the ends of the through holes are sealed alternately as in 20. Because each of the through holes are sealed at one of the ends, the gases that enter through one hole are discharged in another after passing through a partition wall separating the through holes. A schematic depiction of the wall-through gas flow is marked with number 30 (Fig.2).

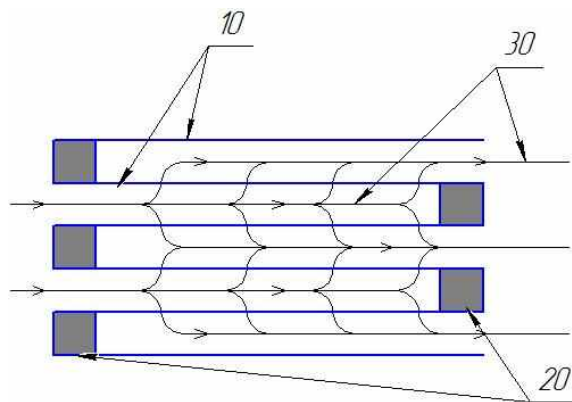


**Figure 2:** Schematic plan view of the reforming element.

The honeycomb structural body is covered on its side wall with a thermal insulation layer, which will prevent heat losses from the reforming element to the reactor tube. If the reforming element is heated by an electrical current running through the element, the insulation layer

must also be dielectric. If the voltage is supplied with one central electrode, the other outer electrode can be connected directly to the reformer tube.

### 2.3 Operation Method

The aim of the device is to perform a controllable burning of the fuel – air – steam mixture. This kind of mixture is not always easy to ignite. This is why the ignition must be of a voluminous type, for example in discharge or active media. In this work a honeycomb structural body was used as an igniter.

The operation of the reforming device is performed in three stages: preheating, start-up and reforming. On the first preheating stage, the reforming member is heated to temperatures of about 800 °C, at least in part with a heater. The heater can be electrical and connected to the honeycomb structural body, or it can be performed by burning the fuel – air mixture in front of the reforming element with an embedded igniter.

At the start-up stage, the fuel–air mixture injection is switched on and it starts to burn at the hot regions of the preheated reformer. Now the entire reformation region will be heated by the heat released from the oxidation reaction. The fuel/air component ratio is adjusted to get the maximum heat from the reaction

The final step is the reforming stage. The fuel, air and steam mixture is adjusted and the amount and quality of the mixture is settled to maintain the proper internal temperature (800-1500 °C) of the reformer to produce maximum yields. The ratio of components should be close to the ideal stoichiometric ratio for partial oxidation reaction. The water-gas shift reaction should also be considered.

The control and switching of operation modes can be carried out by using the devices for temperature and gas composition measurement.

### 2.4 Effect of the Wall-Through Flow

One of the problems of reformation using the partial oxidation reaction or water–gas shift reaction is the flame. The flame propagation velocity usually does not exceed 50 cm/sec. This results in the productivity of the reformer being limited by its geometrical size or cross-section. Catalysts or plasma are often used to accelerate this reaction.

In the present work, the honeycomb structural body with its wall-through flow forms a different burning area. The reforming gas flows not in parallel to the axis as in other reformation devices, but rather in a perpendicular direction to the axis through the porous walls, with the gas velocity much lower than in other parts of the device. This happens because the thin porous walls have low flow resistance relative to the blocked passages and the gas takes the path of lower resistivity, meaning perpendicular to the ceramic walls in 10. of Figure 2. Thus the combustion surface area is as large as the surface area of all the porous walls, tens or hundreds of times greater than the cross-section of the reforming element.

The limit for device productivity in the absence of catalysts can be estimated in the following way. The surface area  $S$  of all the porous walls is first estimated. The flame propagation velocity  $F$  is usually known for each particular reaction. So the volume  $V$  of reactant to be reformed should not be bigger than  $F$  times  $S$ .

$$V < F * S$$

## 3. EXPERIMENT

### 3.1 Procedure

Initially the SiC block was heated through several steps. First, AC 100 V was used for about 10 min. until the temperature become 150-160 °C. After this temperature the resistance of the block decreased to below 100  $\Omega$ . At this moment, current limitation was necessary because fixing the

voltage leads to steep increase of the current and can cause damage to the equipment.

In the next stage DC 70 V – 15 A was connected. It started in a 70 V – 1 A voltage limitation mode, and in a few minutes finished in a 20 V – 15 A current limitation mode at temperatures of about 230 °C. The last power source to be connected was 50 V – 200 A. Using this one we gradually increased current from 15 A to 40 A during 20 min. reaching a temperature of about 550 °C.

The oil spray was then switched on, with fuel and air flow rates about 3 ml/min, and 10 l/min, respectively. The heat from the chemical reaction works together with DC to heat the block. At 800 °C the DC is turned off to prevent overheating.

When the reformer was heated by electric current, the temperature distribution was affected by the current density at the specific region. The area around the central lead was hotter than the other parts while current was being transferred. The temperature was uniform, however, when the reformer was heated by the combustion of sufficient fuel. When the fuel flow rate was low, the temperature of the outlet of the reformer was lower than that of the inlet of the reformer. A part of the mixture then passed through the low temperature region and the reaction was not uniform.

### 3.2 Gas Analysis

For the gas composition measurements we used GASTEC gas analyzing tubes. Hydrogen cannot be detected directly by said tubes because remaining hydrocarbons affect readings to a large degree. We used an indirect method, as disclosed below.

We measured CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O concentrations in the reformed gas. The amount of oxygen was undetected, meaning it was less than 1 %. That gave us the possibility of calculating the total outgoing oxygen as a sum of oxygen in CO, CO<sub>2</sub> and H<sub>2</sub>O. These figures allowed us to estimate the percentage of nitrogen and argon in the mixture, because they have the same ratio as

in air (N<sub>2</sub>+Ar content = 3.77 x O<sub>2</sub> content). By summing CO and CO<sub>2</sub>, we get the amount of carbon totally lost with the hydrogen. After that we can calculate the clean H<sub>2</sub> yield as carbon amount times 1.86 (H/C ratio in soybean oil) and divide by 2 (two atoms in one molecule). From the resulting figure we subtract the water concentration, because some hydrogen is lost in the reaction with oxygen. This final concentration of clean hydrogen in the reformed gas is shown in the table; its value was usually 15.6 – 18.7 %.

### 3.3 Calculations

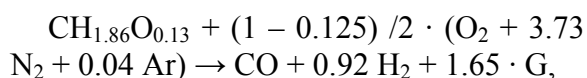
The composition of soybean oil in wt% of organic fractions is as below [1].

C: 75.4; H:11.7; O: 12.9; N: 0.0; S: 0.0.

The reduced formula of the oil is CH<sub>1.86</sub>O<sub>0.13</sub>, and it was used for balance calculations. The density is 0.90 g/ml. To make the O/C ratio equal in this case, the oil to air ratio must be 3:8 if the first one is measuring in ml/m and the last one in l/m.

## 4. RESULTS AND DISCUSSION

For the reformation of the soybean oil to synthesis gas, we used a small reformer with diameters of 20 and 28 mm, surrounded with 0.5 cm thick ceramic wool insulation. The first series of measurements was performed with controlling the CO level on the exit. The degree of reformation was estimated as a ratio of measured CO concentration to the maximum concentration according to the reaction:

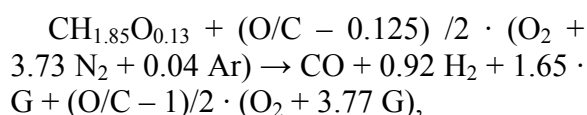


where G is a molecule of balance gases – nitrogen and argon, which are not participating in the reaction.

In this case the O/C ratio is equal and the maximum CO concentration is therefore

28%.

When the amount of the oil exceeds the ideal stoichiometric ratio, a part of the fuel remains untreated. Without a detailed composition study, we can roughly estimate the upper CO concentration as 28%. In an excess of air the reaction is:



and it is therefore easy to compute the resultant maximum CO amount:

$$\text{CO (max)} = 1/(1 + 0.92 + 1.65 + (\text{O/C} - 1)/2 \cdot 4.77) \cdot 100\%.$$

Results of measurements are shown in the Table 1. One can see that a lower O/C ratio results in a higher amount of CO. But at the same time, we measured and controlled the temperature of the external side of the reformation chamber under the outer thermal insulation. This measurement is not indicative of the real reforming temperature, but rather reflected temperature drift with time lag. While the inside of the reformer was sometimes over 1000 °C, the readings on the side were only 600-700 °C. We noticed that an increase of air flow at the same fuel flow, or an abating of fuel at the same air flow leads to a temperature rise of up to 100 degrees. This effect shows that high oxygen concentrations induce high heat

production, and elevating the fuel feed increases the total vaporization heat loss. While the stoichiometric ratio of the components is capable of maintaining a self-sustained reaction, an increase of oil flow can cease the reaction depending on heat fluxes and insulation of heat loss from the reformer. In these circumstances the increased reformation of the rich mixture can be explained with the fact that the portion of supplied carbon converted into CO remains at nearly the same level of 20-25 %, and the increased oil relative to air enlarges the CO concentration. The percentage of carbon to CO conversion coincides with  $\text{CO}/\text{CO}_{\text{max}}$  when  $\text{O/C} > 1$ , and is equal to  $\text{CO}/\text{CO}_{\text{max}} \cdot \text{O/C}$  otherwise.

Another remarkable conclusion can be made from the graph. The reformation efficiency depends only on the O/C ratio, while the total amount of the mixture has much less effect (within the accuracy of the measurements).

Carbon that was not converted to CO was converted to CO<sub>2</sub> and light hydrocarbons. CO<sub>2</sub> is useless in energy production, but we found its concentration was quite high compared to the case of diesel fuel.

Occasional increases of temperature in the reformer above 1000 °C created some problems with the internal electrical contacts

Table 1. Reformation with 20 mm diameter labyrinth block.

| No | Oil, sccm | Air, l/m | O/C  | CO, vol % | CO <sub>2</sub> , vol % | CO <sub>max</sub> , vol % | CO/CO <sub>max</sub> , % | CO/C, % |
|----|-----------|----------|------|-----------|-------------------------|---------------------------|--------------------------|---------|
| 1  | 20        | 24       | 0.53 | 13        | 10.5                    | 28.0                      | 46                       | 24.4    |
| 2  | 15.4      | 24       | 0.65 | 11        | 7                       | 28.0                      | 39                       | 25.4    |
| 3  | 11        | 24       | 0.85 | 7         | 9                       | 28.0                      | 25                       | 15.2    |
| 4  | 6.9       | 15       | 0.85 | 5         |                         | 28.0                      | 18                       | 21.3    |
| 5  | 6.9       | 20       | 1.09 | 7         |                         | 26.4                      | 27                       | 26.5    |
| 6  | 3         | 10       | 1.23 | 5         |                         | 24.2                      | 21                       | 20.6    |
| 7  | 3         | 15       | 1.79 | 4         |                         | 18.4                      | 22                       | 21.8    |

Table 2. Reformation with 28 mm diameter labyrinth block.

| No | Oil, ccm | Air, l/m | O/C  | CO, vol % | CO <sub>2</sub> , vol % | H <sub>2</sub> O, vol% | CO <sub>max</sub> , vol% | H <sub>2</sub> ,(calc) vol% | CO/CO <sub>max</sub> , % | CO/C, % |
|----|----------|----------|------|-----------|-------------------------|------------------------|--------------------------|-----------------------------|--------------------------|---------|
| 9  | 15.4     | 10       | 0.34 | 13        | 9                       | 2.0                    | 28                       | 18.6                        | 46                       | 16.0    |
| 10 | 11.0     | 12.5     | 0.45 | 13        | 12                      | 2.2                    | 28                       | 24.9                        | 46                       | 12.9    |
| 11 | 15.4     | 15       | 0.51 | 8         | 8                       | 2.7                    | 28                       | 12.2                        | 29                       | 23.5    |
| 12 | 6.9      | 10       | 0.58 | 11        | 11.5                    | 2.7                    | 28                       | 18.3                        | 39                       | 26.9    |
| 13 | 11.0     | 15       | 0.61 | 13        | 10                      | 2.7                    | 28                       | 18.8                        | 46                       | 24.0    |
| 14 | 6.9      | 15       | 0.85 | 7         | 12                      | 2.2                    | 28                       | 18.3                        | 25                       | 21.3    |
| 15 | 3.0      | 10       | 1.23 | 8         | 11.5                    | 2.7                    | 24.2                     | 15.5                        | 33                       | 33.0    |
| 16 | 6.9      | 35       | 1.82 | 4         |                         |                        | 18.1                     |                             | 22                       | 22.1    |

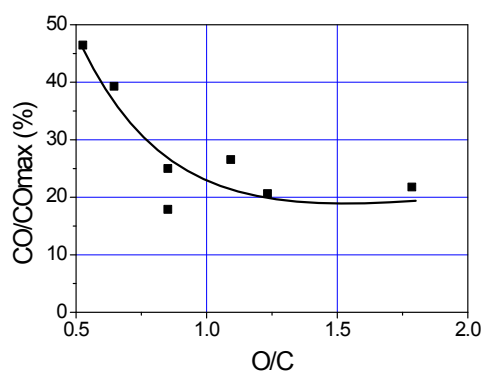


Figure 3: CO content in reformed gas (20 mm labyrinth block).

leading to the side wall of the reformer. In later experiments the reformer was pressed into the chamber directly, without insulation and with direct electrical contact.

Results of this experiment can be seen in Table 2 and Fig.4. The greater surface of reforming in the 28mm diameter block results in higher CO concentrations. However, the proportion of carbon

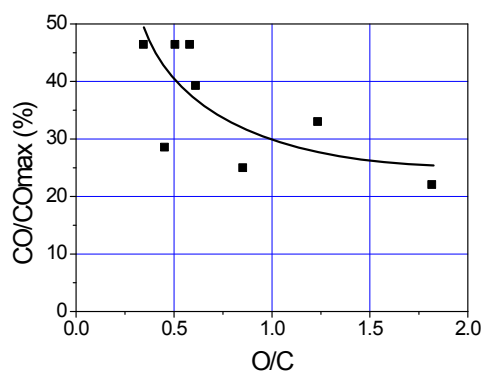


Figure 4: CO content in reformed gas (28 mm labyrinth block).

converted into CO gas increases to a level of 20-30%.

The correlation of with experimental parameters is difficult to deduce. At high O/C ratios, the concentration of carbon dioxide at the exit exceeds that of carbon monoxide because of abundant free oxygen. At higher temperatures, H<sub>2</sub>O and CO<sub>2</sub> become less stable than H<sub>2</sub> and CO, so an increase of temperature in the reaction region would be useful.

The amount of water in the gas is usually about 2-3%. This means that hydrogen released from the reaction of carbon and oxygen (CO+CO<sub>2</sub> consists of about 20 % of the reformed gas) does not completely transfer into water. Taking the amount of carbon in these compounds, the H<sub>2</sub> amount in the resultant reformed gas can be estimated using the H/C ratio of the oil. Finally, the water quantity must be extracted from the total released hydrogen.

Conc.(H<sub>2</sub>) ~

$$\text{Conc.}(\text{CO}+\text{CO}_2) \cdot 1.86 / 2 - \text{Conc.}(\text{H}_2\text{O}).$$

This calculated value was 12-25 % (Table 2). That means that supplying the reformer with 10 ml/min of vegetable oil we about 2 l/min of H<sub>2</sub>; using it as fuel for a

fuel cell, we can get about 300 W of electrical power.

## 5. CONCLUSION

We designed a new small-scale device for organic fuel reformation. One of its peculiarities is the active portion of the reformer, which has a honeycomb wall-through flow structure that turns the flow of the fuel-air mixture. The high surface area of this structure leads to an increase of the flame front surface area and a decrease of the local gas speed in the reformation region. The system does not use any catalysts and thus it is not sensitive to fuel impurities.

Reformation of soybean oil shows a 20-30% conversion of carbon into CO, and the CO concentration reaches 13 % of the outgoing gas. By calculations, about 16 vol % of hydrogen was expected in the reformed gas.

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