

PROGRESS IN DEVELOPMENT AND COMMERCIALIZATION OF BASE-FACILITATED REFORMING (BFR) TECHNOLOGY

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1. Introduction

Energy Conversion Devices, Inc. (ECD) has developed a new reformation process for production of hydrogen from organic fuels. The process uses base material such as sodium hydroxide as a reactant in the reformer. This base-facilitated reforming (BFR) process has several advantages over conventional steam reforming. The process has been demonstrated on a variety of fuels, in particular methanol and ethanol, showing reformation occurring at significantly lower temperatures compared to steam reformation of the same fuels. It yields higher purity hydrogen in a one-step process without formation of CO or CO₂, a greenhouse gas. Additionally, we have studied reformation of solid biomass materials using the BFR process. A variety of biomass feedstocks such as starch, wood, grass and more can be reformed at temperatures of 200°C-300°C in a one-step reaction without the need for high temperature gasification. Economic analysis has shown using biomass as feedstock lowers the cost of hydrogen produced in the BFR process to below \$2.0/kg H₂. ECD is working on commercialization of the BFR process for biomass reformation commercialization in distributed hydrogen generation.

2. Base-Facilitated Reforming (BFR)

A schematic representation of the base-facilitated reforming (BFR) process in comparison to conventional steam reforming (SR) process is shown in fig 1.

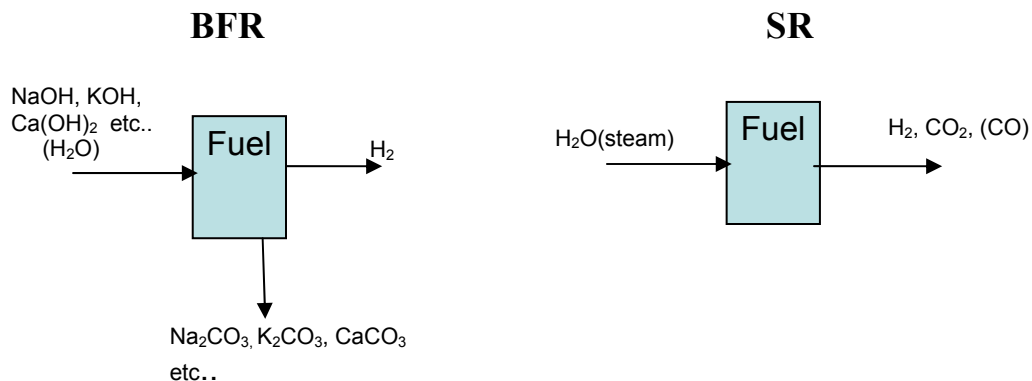
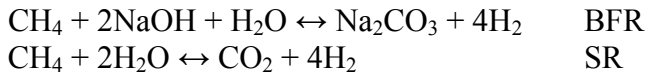


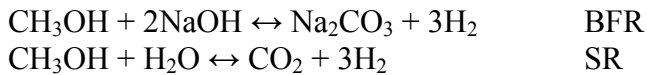
Figure 1. Schematic representation of the BFR process
Vs. conventional steam reforming (SR) process

In the base-facilitated process, base material is reacting with fuel to form pure hydrogen and solid carbonate. This is in contrast to conventional steam reforming where steam at high temperature is reacting with fuel to form a mixture of gases which include CO and CO₂ in addition to hydrogen. The chemistry associated with the base-facilitated Reforming (BFR) process is described in the following equations and compared to steam reforming (SR) process for various fuels. The chemistries of other fuels are similar.

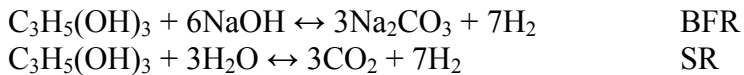
Methane (CH₄)



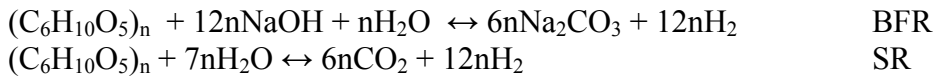
Methanol (CH₃OH)



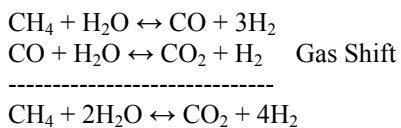
Glycerol (C₃H₅(OH)₃)



Cellulose (C₆H₁₀O₅)_n



In base-facilitated reforming (BFR), the hydrogen is produced in a one-step process. In contrast, the steam reforming (SR) is a multi-step process where carbon monoxide (CO) is formed in the first stage of the reaction. The CO is then reacted in the second stage, the water-gas shift reaction (WGS), to form carbon dioxide (CO₂) and additional hydrogen. Hydrogen is then separated from the CO₂ by the pressure swing absorption (PSA) process. An example of the different stages of the steam reforming process is shown for methane fuel below.



Flow diagrams representations of steam reforming and base-facilitated processes are shown in figure 2 below.

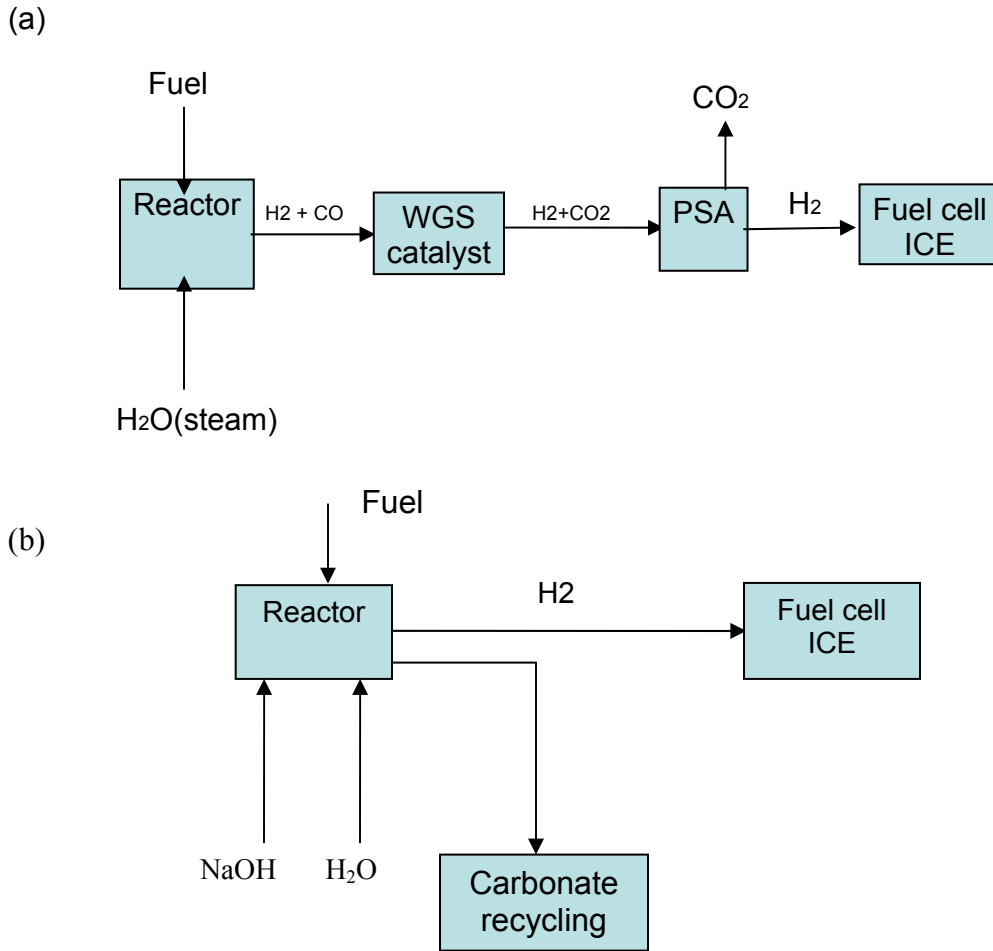


Figure 2. Flow diagram representation of (a) steam reforming (b) base-facilitated reforming

In addition to BFR being a simpler process, it operates at lower temperatures and requires less heat for operation. This is because of more favorable thermodynamic properties compared to the steam reforming reaction. As table I shows, the Gibbs free energies (ΔG°) of the BFR reactions are lower than that of the SR reactions for different fuels, resulting in lower reaction temperatures for the BFR processes. Table II shows the enthalpies (ΔH°) of the BFR reactions are lower than their associated SR processes resulting in lower heat required for operation and higher thermal efficiency.

Table I. Gibbs Free Energies (ΔG°) and reaction temperatures of different fuels in the BFR and SR Processes

Fuel	ΔG° (Kcal/mole)	Reaction temperature (oC)
CH ₄ (SR)	+31.2	900
CH ₄ (BFR)	+0.55	300
CH ₃ OH (SR)	+2.2	350
CH ₃ OH (BFR)	-28.5	120
C ₂ H ₅ OH (SR)	+23.3	800
C ₂ H ₅ OH (BFR)	-38.3	130
C ₆ H ₁₂ O ₆ (SR)	-8.2	900
C ₆ H ₁₂ O ₆ (BFR)	-192	220

Table II. Enthalpies (ΔH°) and thermal efficiencies of different fuels in the BFR and SR processes

Fuel		ΔH° (Kcal/mole)	Efficiency(%)
CH ₄ (SR)	Methane	+60.5	92
CH ₄ (BFR)	“	+12.9	113
CH ₃ OH (SR)	Methanol	+31.5	94
CH ₃ OH (BFR)	“	-9.7	114-121
C ₂ H ₅ OH (SR)	Ethanol	+83.3	92
C ₂ H ₅ OH (BFR)	“	+1.0	117
C ₆ H ₁₂ O ₆ (SR)	Glucose	+150.2	92
C ₆ H ₁₂ O ₆ (BFR)	“	-96.8	114-136
C ₁₂ H ₂₂ O ₁₁ (SR)	Sucrose	+213.4	91
C ₁₂ H ₂₂ O ₁₁ (BFR)	“	-291.3	112-136
C ₆ H ₁₀ O ₅ (SR)	Cellulose	+146.1	90
C ₆ H ₁₀ O ₅ (BFR)	“	-169.3	112-153

3. Test Results of Reforming in the BFR Process

ECD has demonstrated the BFR process in variety of liquid or solid fuels. Examples of fuels which were successfully reformed using the BFR process are:

Alcohols: Methanol, Ethanol, Crude Ethanol, E95, Ethylene Glycol, Glycerol (by-product from bio-diesel production)

Sugars: Glucose, Fructose, Starch (Cornstarch, Potato starch)

Fossil Fuels: Coal

Biomass: Grass, Sawdust, Woodchips, Corn, Potato Peels, Cellulose, Hemicelluloses (Xylan from Beachwood), Lignin (Organosolv)

Municipal

Solid Waste: Paper

Some of the fuels reformed using the BFR process are shown in figure 3 below

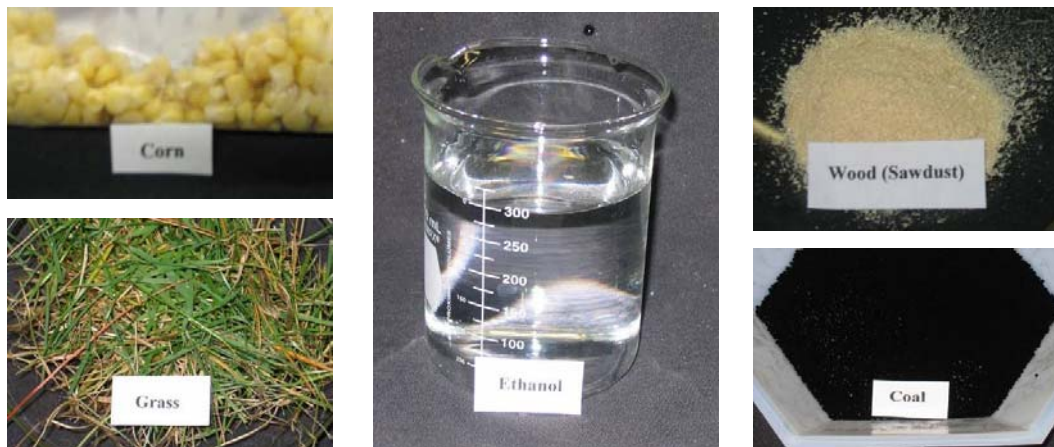


Figure 3. Examples of fuels reformed using ECD's BFR process

In all cases reformation using the BFR process occurred at significantly lower temperatures than the counterpart SR of the same fuels.

(a) Liquid fuels

Liquid fuels such as methanol, ethanol and glycerol could be reformed at low temperatures where liquid phase reforming is possible. Results of reforming these fuels in the liquid phase are shown in Figures 4-6

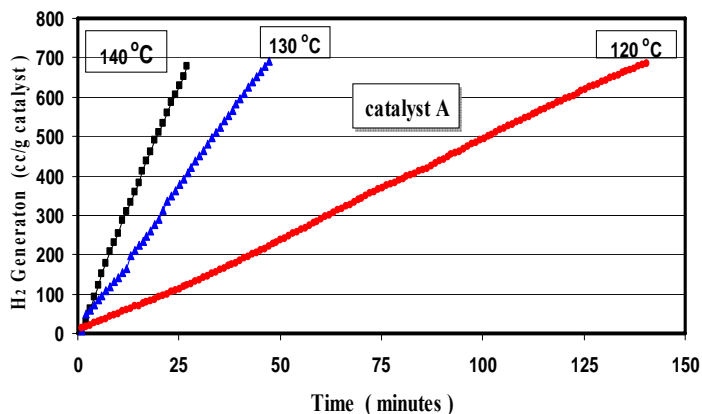


Figure 4. Base Facilitated Reforming of methanol at different temperatures in a liquid phase batch reactor – 150 psi reactor pressure

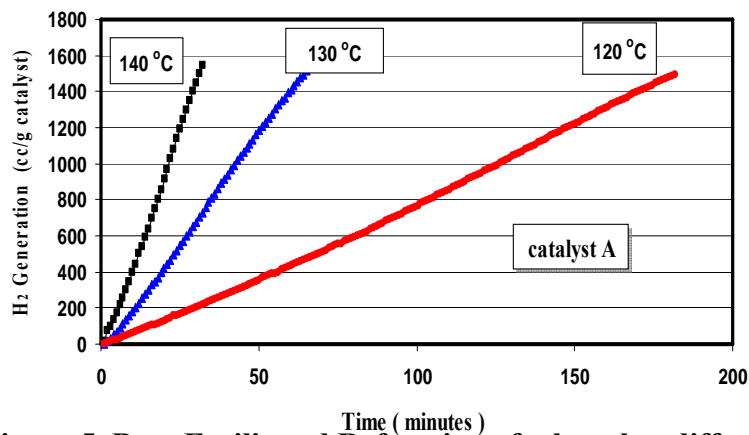


Figure 5. Base Facilitated Reforming of ethanol at different temperatures in a liquid phase batch reactor – 150 psi reactor pressure

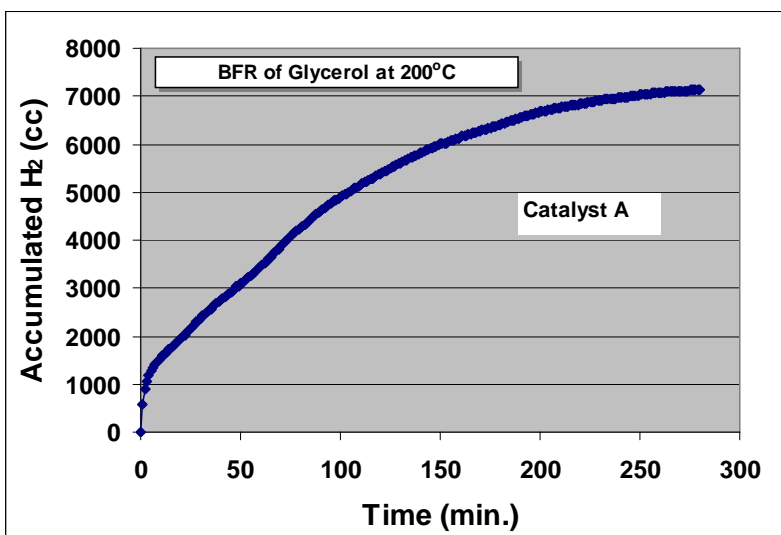


Figure 6. Base Facilitated Reforming of glycerol at 200°C in a liquid phase batch reactor – 150 psi reactor pressure

(b) Solid biomass feedstocks

Laboratory experiments at ECD have shown that reforming of solid biomass materials using the BFR process is also possible. Figures 7 and 8 show test results of reforming some cellulosic biomass feedstocks in their raw unpurified state.

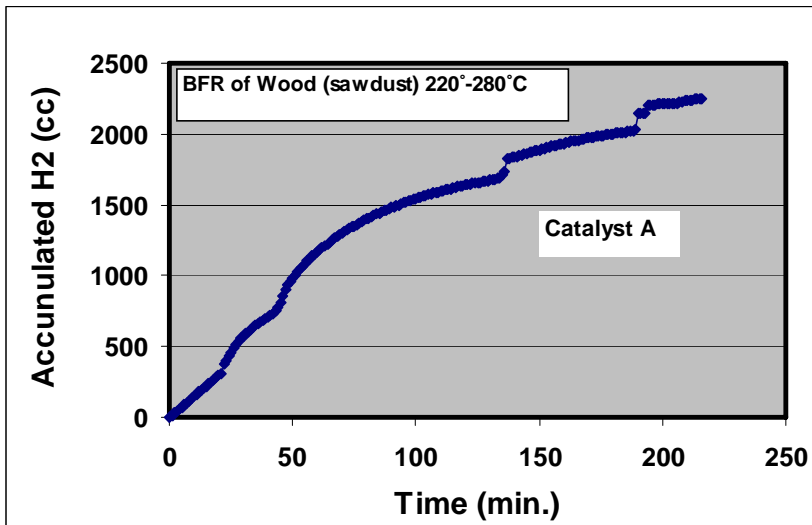


Figure 7. Base facilitated reforming of wood in a batch process-150 psi reactor pressure

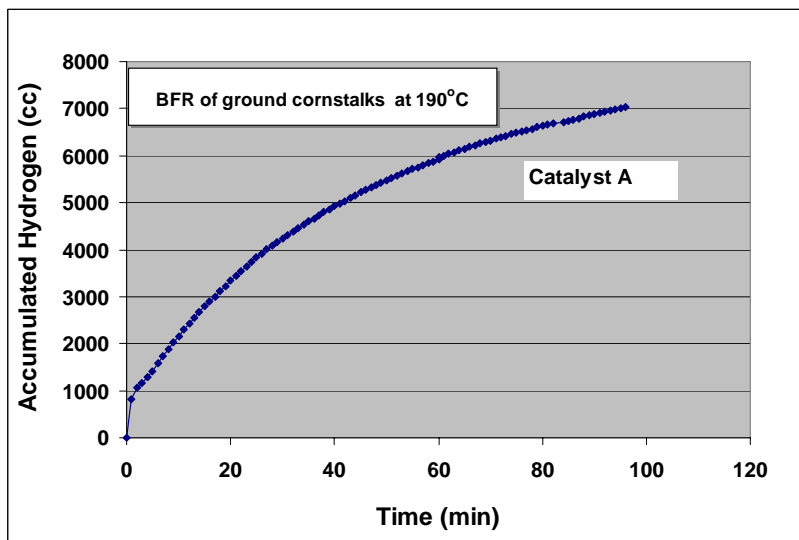


Figure 8. Base facilitated reforming of cornstalks in a batch process-150 psi reactor pressure

The hydrogen yield obtained in the reformation of these feedstocks was close to 100% and the biomass material reacted close to completion. Separate experiments reforming different components of cellulosic feedstocks namely

cellulose, hemicellulose and lignin in their pure state show each of these components can be reformed using the BFR process. This is shown in figure 10. The reformation of the individual components was also close to completion with hydrogen yield of ~100%.

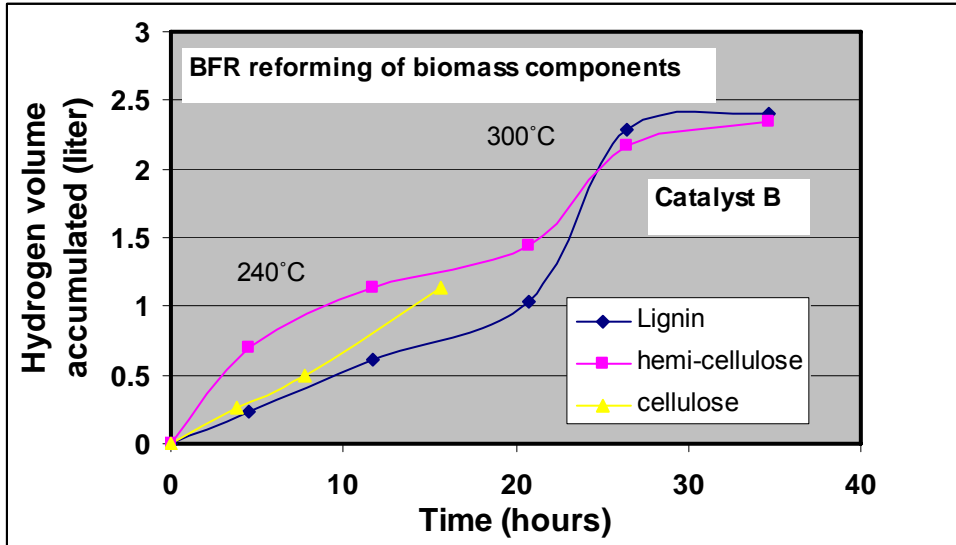


Figure 9. Base facilitated reforming of biomass components in a batch process-150 psi reactor pressure

4. Economics of the BFR process

Economic evaluation of the BFR process using the H2A economic analysis tool developed by Department of Energy (DOE) was conducted. H2A uses the following conditions and input sources:

- Net present value with Internal Rate of Return (IRR): 10%
- 20 years depreciation on facility equipment
- 10 years depreciation on reactor
- Cost of feedstock and electricity taken from Energy Information Administration (EIA) Annual Energy Outlook report

Analysis showed the cost of hydrogen produced using the BFR process is highly sensitive to the cost of the feedstock used. The lowest cost is obtained when biomass is used as the feedstock as seen in figure 10.

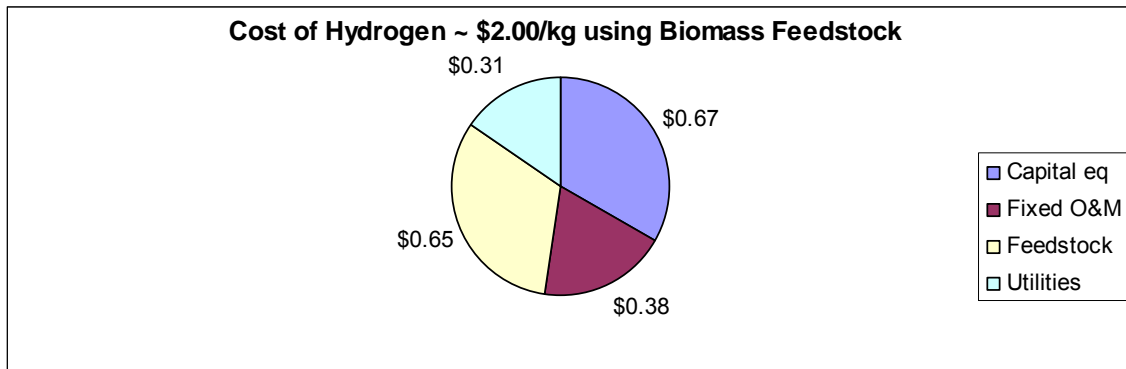


Figure 10. Cost structure for hydrogen using BFR process and biomass feedstock at production rate of 1,500 Kg/day H₂

For comparison, the cost of hydrogen using methanol and ethanol as fuels was calculated to be \$2.50/kg and \$3.60/kg respectively. In these calculations, the cost of recycling the sodium carbonate (Na₂CO₃) by-product was taken into consideration. The cost of producing hydrogen from biomass is competitive with the DOE goal of \$2-\$3/kg and with the current cost of delivered (merchant) hydrogen (>\$10/kg).

5. Progress Towards Commercialization

(a) Reactors

The advantages the base-facilitated reforming provides the ability to produce hydrogen in small distributed manner, the ability to reform variety of fuels and in particular biomass materials, lower reforming temperatures and lower energy consumption, no emission of CO and CO₂ and very competitive cost. ECD is working towards commercialization of the process for biomass reforming. ECD has built and tested small batch reactors to process liquid or solid feedstocks (figure 11 (a,b)) and continuous liquid flow reactor that produces 200 gr H₂/day from liquid fuels (methanol, ethanol) has been demonstrated (figure 11(c)). A fluidized bed prototype reactor that will process solid biomass feedstock having the capability to produce 10 Kg H₂/day has been built (figure 12) and initial testing has begun. A pilot line to produce 20 kg H₂/day is planned as the next stage to demonstrate large scale process. Successful demonstration of larger scale biomass processing will lead to commercialization of the process in 3-5 years.

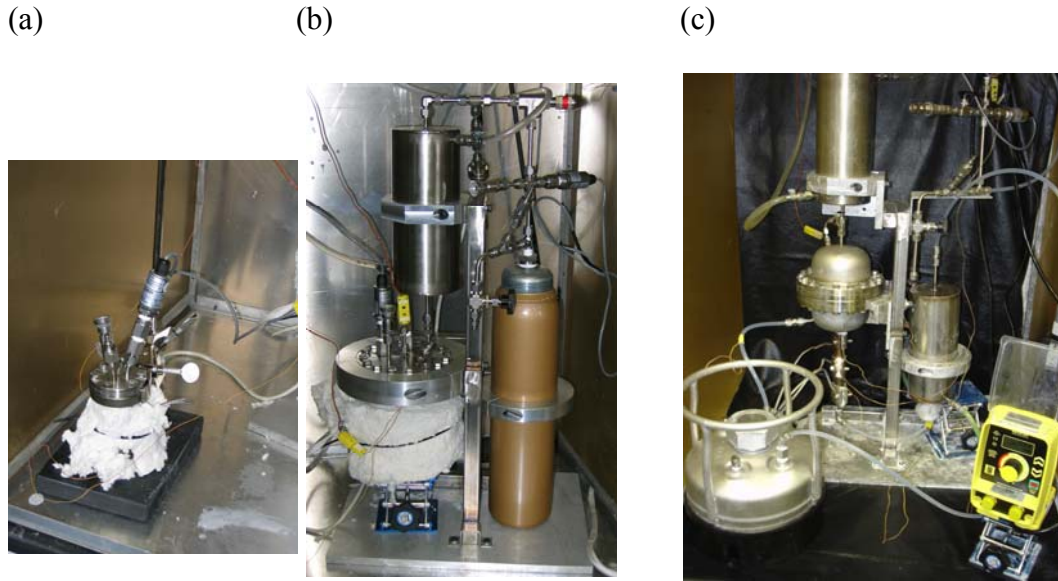


Figure 11. Batch BFR reactors: (a) 3L H₂/hr, 0.5 hrs (b) 10L H₂/hr, 8 hrs and (c) continuous flow reactor 100 L/hr



Figure 12. Prototype 10 kg H₂/day solid biomass reactor

(b) **By-Product (carbonate) recycling**

Base-facilitated reforming produces highly pure hydrogen and solid carbonate (i.e. Na_2CO_3) as the by-product. For the process to be economically viable, the solid carbonate has to be recycled back to the alkaline material (i.e. NaOH) for re-use in the reforming process. Although other alternative are considered such as: disposal of the carbonate to sequester the CO_2 , use the carbonate to generate pure CO_2 for various industrial applications or sell the carbonate for various industrial applications (i.e. glass), recycling appears to be the most economical option. The economic analysis of hydrogen production cost described earlier took in consideration the cost of recycling. Recycling of sodium carbonate is a known process used in the paper mill industry in the pulping process (Kraft Process). The chemistry of the process follows the series of equations below:

- (1) $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + 2\text{NaOH}$
- (2) $\text{CaCO}_3 \xrightarrow{\text{heat}} \text{CaO} + \text{CO}_2$
- (3) $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$

Sodium hydroxide (NaOH) is formed in reaction (1) and brought back to the reformer for re-use. The CaCO_3 formed as a precipitate can be decomposed as described in equation 2 by heating to 850°C (calcination) and the CaO formed is converted by hydration (equation 3) back to $\text{Ca}(\text{OH})_2$. This process is known also as recausticizing. The recovery of the NaOH in the Kraft process is $>99\%$. The process can be conducted in sequence to the reforming process. A flow diagram for the reforming process which includes the recycling process is described in figure 13 below. Figure 14 shows flow diagram for the calcinations and hydration processes.

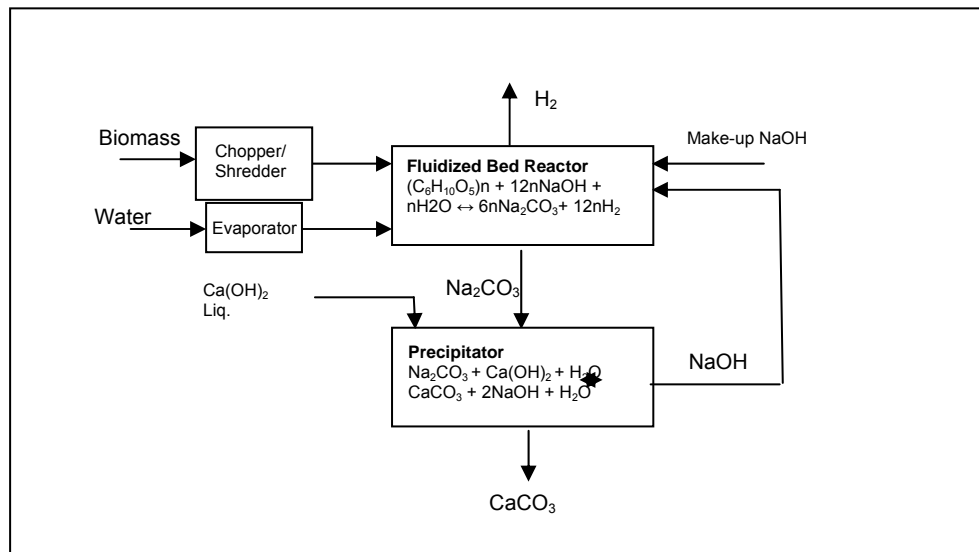


Figure 13. Flow diagram of Na_2CO_3 recycling process

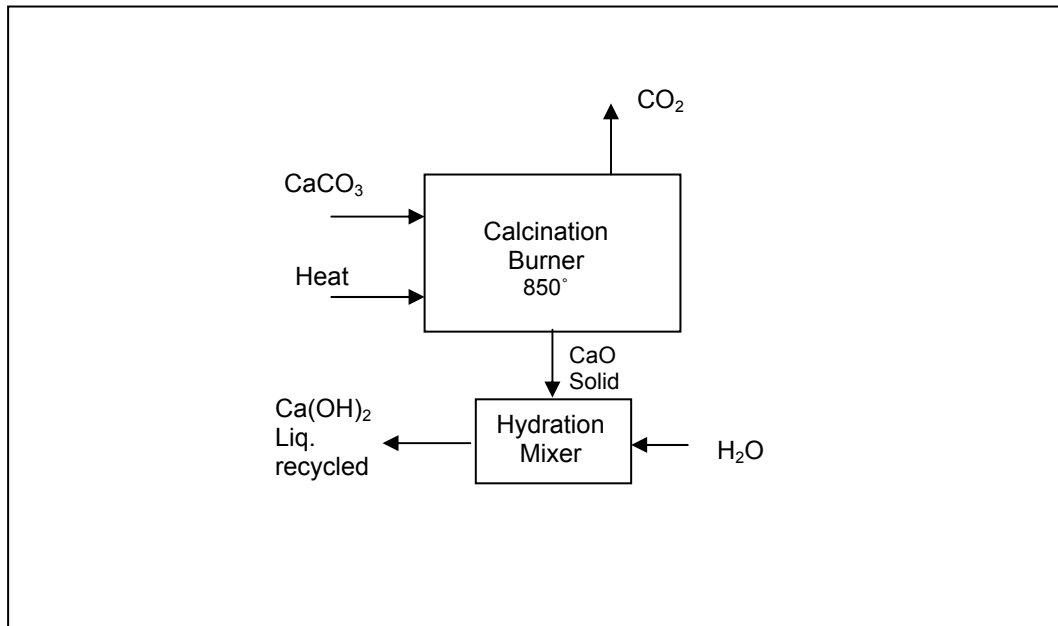


Figure 14. Flow diagram of calcination and hydration processes

16. Summary

We have demonstrated the Base-Facilitated Reforming (BFR) process on variety of fuels. High conversion (close to 100%) of raw biomass feedstocks in unpurified state was obtained using the BFR process with high yield (close to 100%) of hydrogen produced. The process operates at low temperatures of $<300^{\circ}\text{C}$ without generation of CO and CO_2 gases and is economically feasible. Commercialization of the BFR process is underway.