Progress in Development and Commercialization of Base-Facilitated Reforming Technology

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Base-Facilitated Reformation (BFR)

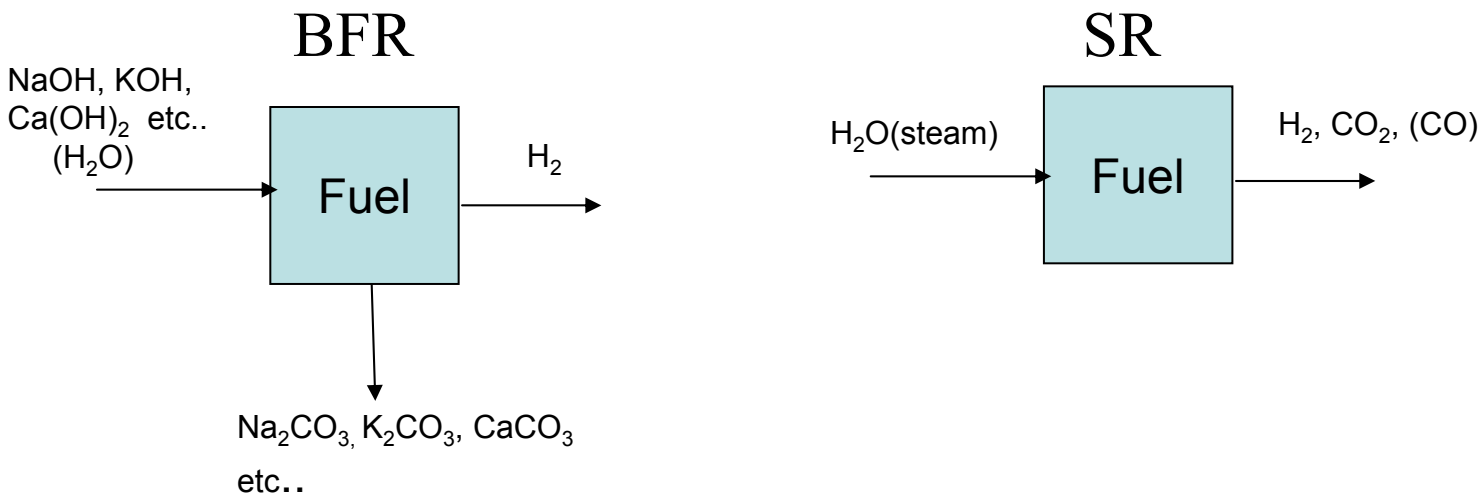
- What is the BFR process?
- BFR reforming-test results
  - Liquid fuels
  - Solid fuels (Biomass)
- Economics
- Work toward commercialization
- By-Product (carbonate) recycling
- Summary

Base-Facilitated Reformation (BFR)

- What is the BFR process?

What is Base-Facilitated Reforming (BFR)?

- Alkaline material is used as a reactant in the reformation process
- Carbonate is formed as a product instead of CO_2



Example – Methane (CH_4)

Base-Facilitated Reforming

$$CH_4 + 2NaOH + H_2O \leftrightarrow Na_2CO_3 + 4H_2$$

Steam Reforming

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$$

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$ Gas Shift

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

Example – Methanol (CH_3OH)

Base-Facilitated Reforming

$$CH_3OH + 2NaOH \leftrightarrow Na_2CO_3 + 3H_2$$

Steam Reforming

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$$

$CH_3OH \leftrightarrow CO + 2H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$ Gas Shift

$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$

Example – Ethanol (C_2H_5OH)

Base-Facilitated Reforming

$$C_2H_5OH + 4NaOH + H_2O \leftrightarrow 2Na_2CO_3 + 6H_2$$

Steam Reforming

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$$

$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2$

$2CO + 2H_2O \leftrightarrow 2CO_2 + 2H_2$ Gas Shift

$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$

Example – Glycerol ($C_3H_5(OH)_3$)

Base-Facilitated Reforming

$$C_3H_5(OH)_3 + 6NaOH \leftrightarrow 3Na_2CO_3 + 7H_2$$

Steam Reforming

$$C_3H_5(OH)_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2$$

$C_3H_5(OH)_3 \leftrightarrow 3CO + 4H_2$

$3CO + 3H_2O \leftrightarrow 3CO_2 + 3H_2$ Gas Shift

$C_3H_5(OH)_3 + 3H_2O \leftrightarrow 2CO_2 + 6H_2$

Example – Glucose $(C_6H_{12}O)_6$

Base-Facilitated Reforming

$$C_6H_{12}O_6 + 12NaOH \leftrightarrow 6Na_2CO_3 + 12H_2$$

Steam Reforming

$$C_6H_{12}O_6 + 6\,H_2O \leftrightarrow 6CO_2 + 12H_2$$

$C_6H_{12}O_6 \leftrightarrow 6CO + 6H_2$

$6CO + 6H_2O \leftrightarrow 6CO_2 + 6H_2$ Gas Shift

$C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 6H_2$

Example – Cellulose $(C_6H_{10}O_5)_n$

Base-Facilitated Reforming

$$(C_6H_{10}O_5)_n + 12nNaOH + nH_2O \leftrightarrow 6nNa_2CO_3 + 12nH_2$$

Steam Reforming

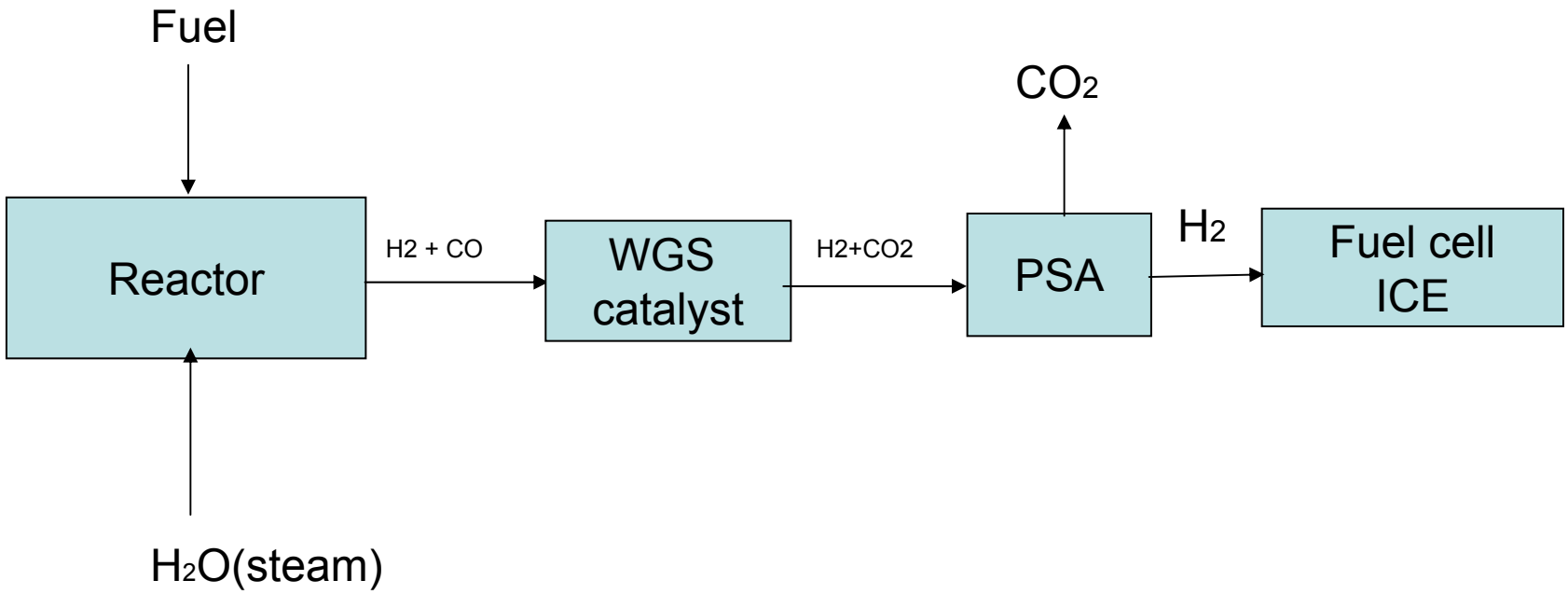
$$(C_6H_{10}O_5)_n + 7nH_2O \leftrightarrow 6nCO_2 + 12nH_2$$

$(C_6H_{10}O_5)_n + nH_2O \leftrightarrow 6nCO + 6nH_2$

$6nCO + 6nH_2O \leftrightarrow 6nCO_2 + 6nH_2$ Gas Shift

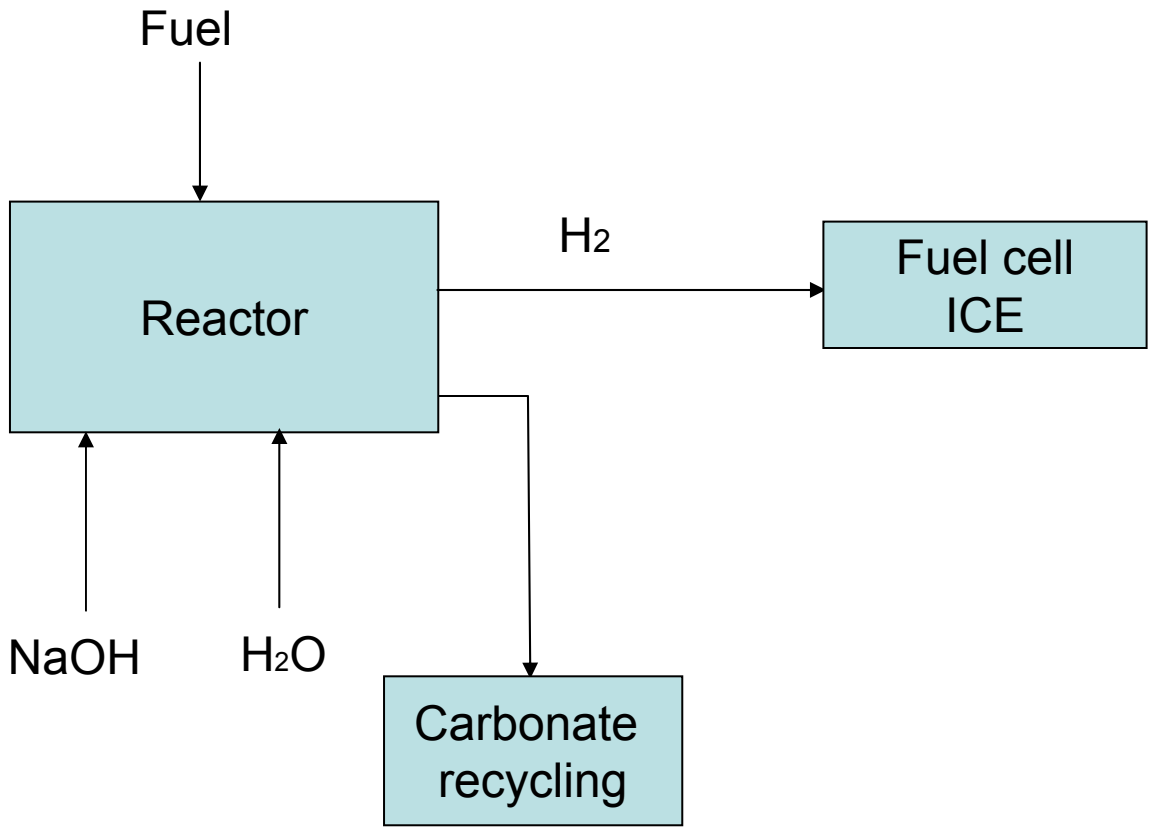
$(C_6H_{10}O_5)_n + 7nH_2O \leftrightarrow 6nCO_2 + 12nH_2$

Steam Reforming Process



Base-Facilitated Reformation Process

Simple One Step Reaction-High Purity Hydrogen



Base-Facilitated Reforming – More Favorable Thermodynamics/ Lower Operating Temperatures

Gibbs free energies ΔG° are significantly lower in the BFR process compared to Steam Reforming – Lower reaction temperatures

Fuel	Δ G° (Kcal/mole)	Reaction temperature (°C)
CH_4 (SR)	+31.2	900
CH_4 (BFR)	+0.55	300
CH_3OH (SR)	+2.2	350
CH_3OH (BFR)	-28.5	120
C_2H_5OH (SR)	+23.3	800
C_2H_5OH (BFR)	-38.3	130
$C_6H_{12}O_6$ (SR)	-8.2	900
$C_6H_{12}O_6$ (BFR)	-192	220

Base-Facilitated Reforming – More Favorable Thermodynamics/ Lower Heat Requirement

Enthalpies ΔH° are significantly lower in the BFR process compared to Steam Reforming – Lower heat of reaction and higher efficiencies

Fuel		ΔH°(Kcal/mole)	Efficiency(%)
CH_4 (SR)	Methane	+60.5	92
CH_4 (BFR)	"	+12.9	113
CH_3OH (SR)	Methanol	+31.5	94
CH_3OH (BFR)	"	-9.7	114-121
C_2H_5OH (SR)	Ethanol	+83.3	92
C_2H_5OH (BFR)	"	+1.0	117
$C_6H_{12}O_6$ (SR)	Glucose	+150.2	92
$C_6H_{12}O_6$ (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
$C_6H_{10}O_5$ (SR)	Cellulose	+146.1	90
$C_6H_{10}O_5$ (BFR)	"	-169.3	112-153

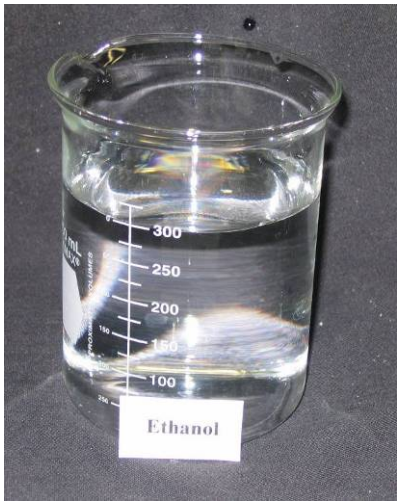
Advantages of BFR Process -Summary

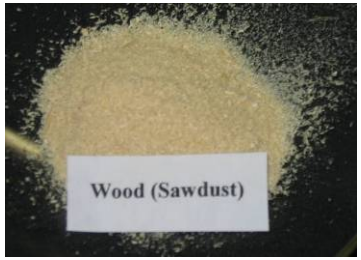
- One step reaction – making reformer design simpler
- No CO or CO_2 gases formed – Gas shift and PSA not necessary. Pure hydrogen is formed.
- Greener process – CO_2 sequestered as Na_2CO_3
- Lower operating temperatures. Operation in liquid phase is possible.
- Batch or continuous operation possible
- Lower heat (ΔH°) required for reforming so more efficient and less expensive operation
- Can be used to reform variety of fuels. Reforming renewable fuels is possible.

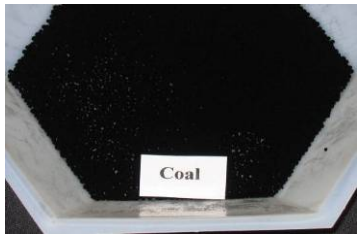
Base-Facilitated Reformation (BFR)

- BFR reforming-test results
  - Liquid fuels
  - Solid fuels (Biomass)

Ovonic Process Reforms Multiple Fuels







Examples of Fuels Reformed by Ovonic Base-Facilitated Reformation

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

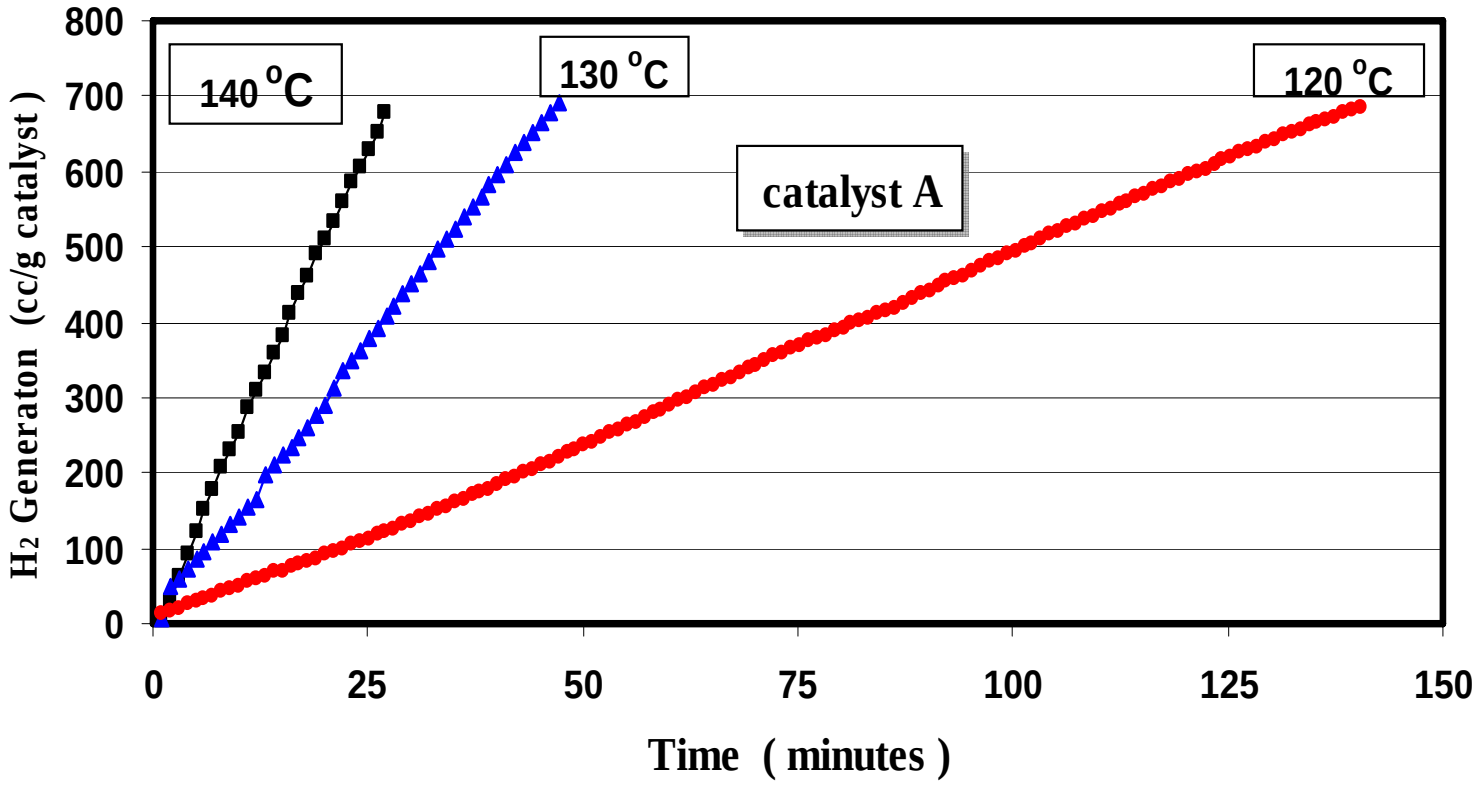
Sugars, Starch: Glucose, Fructose, Starch (Cornstarch, Potato starch)

Fossil Fuels: Methane, Coal

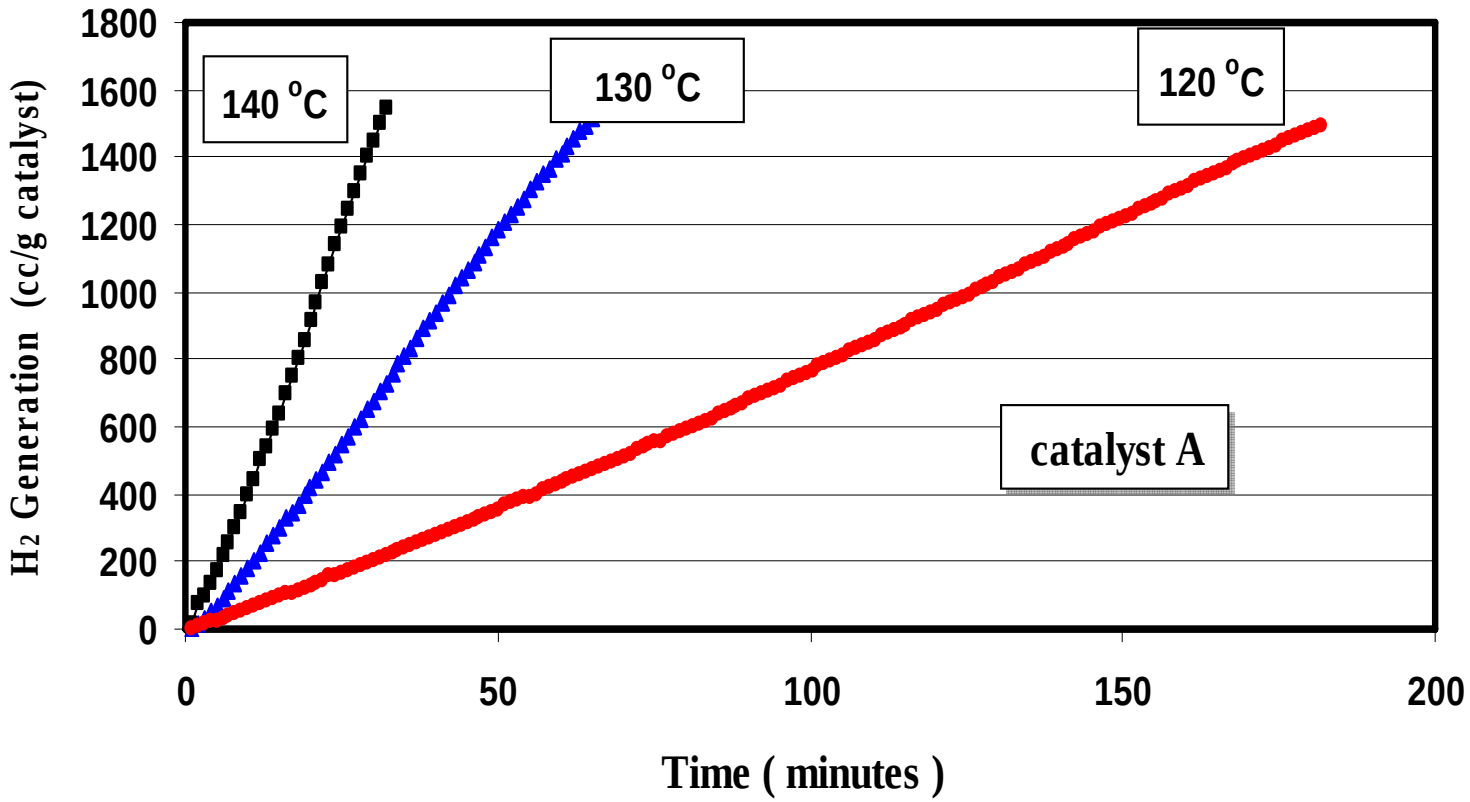
Biomass: Grass, Sawdust, Woodchips, Corn, Potato Peels, Cellulose, Hemicelluloses (Xylan from Beachwood), Lignin (Organosolv)

Municipal Solid Waste: Paper

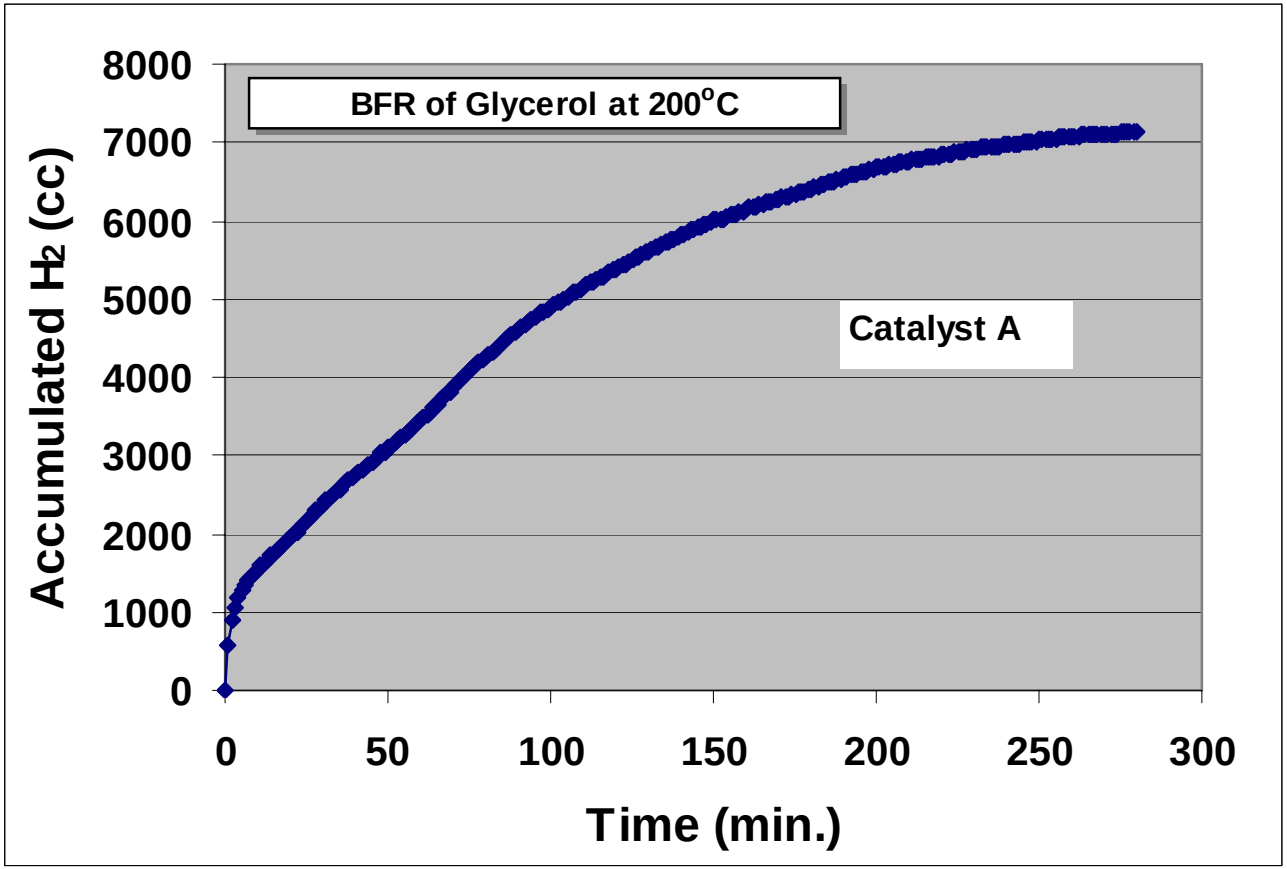
Base-Facilitated Methanol Reformation
Dependence on temperature - Batch Reactor



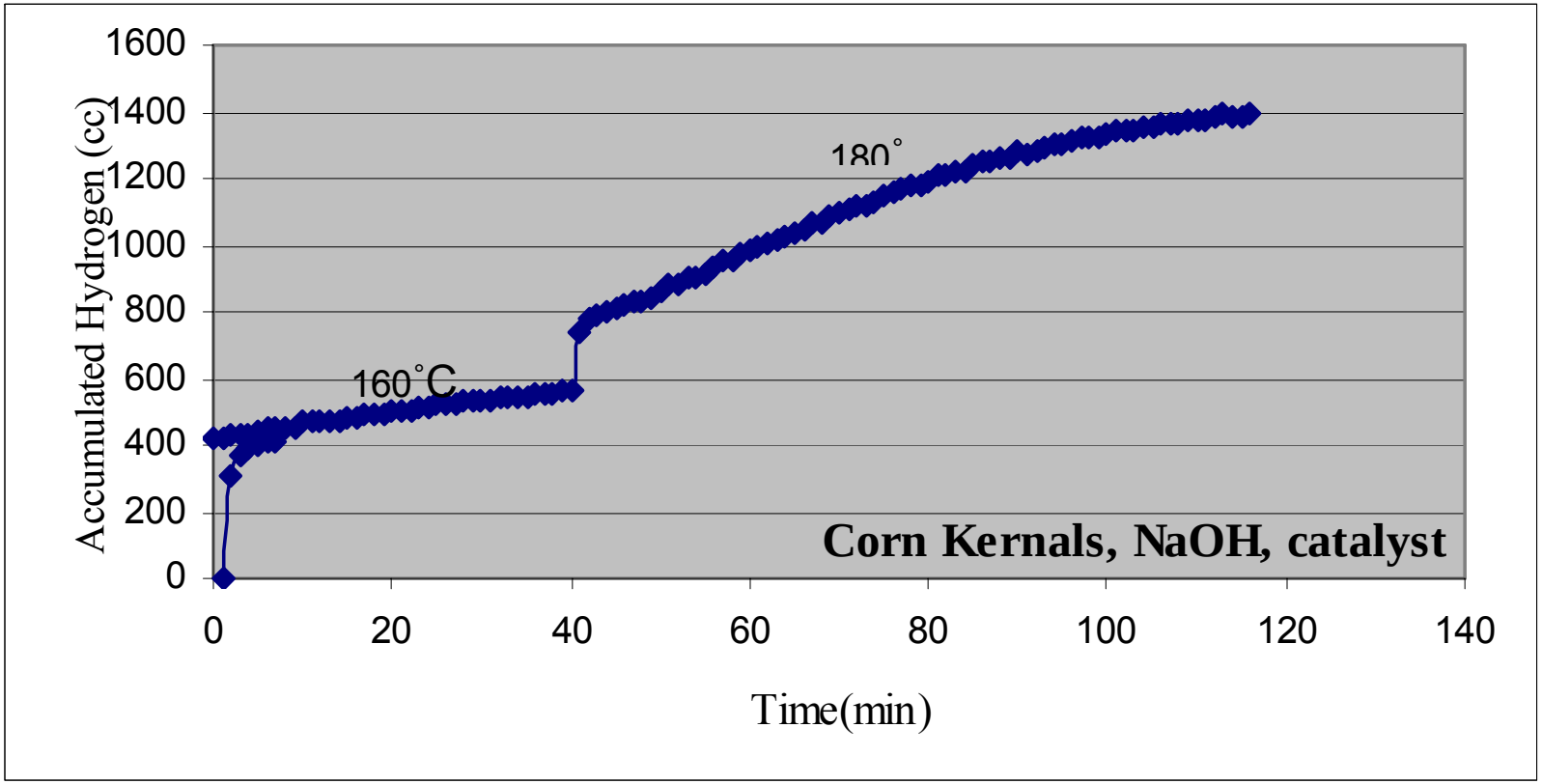
Base-Facilitated Ethanol Reformation
Dependence on temperature - Batch Reactor



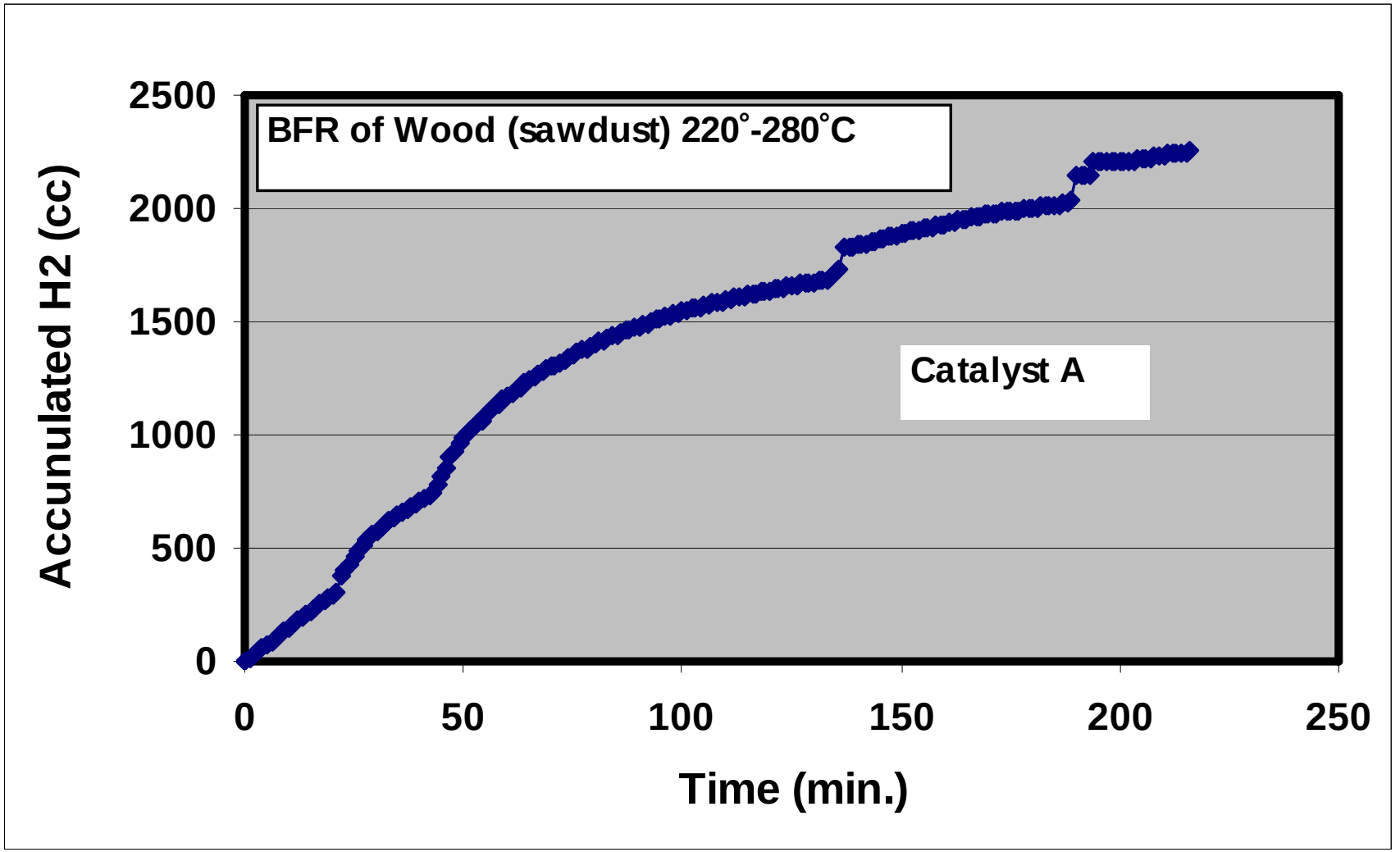
Base-Facilitated Reformation of Glycerol - Batch Reactor



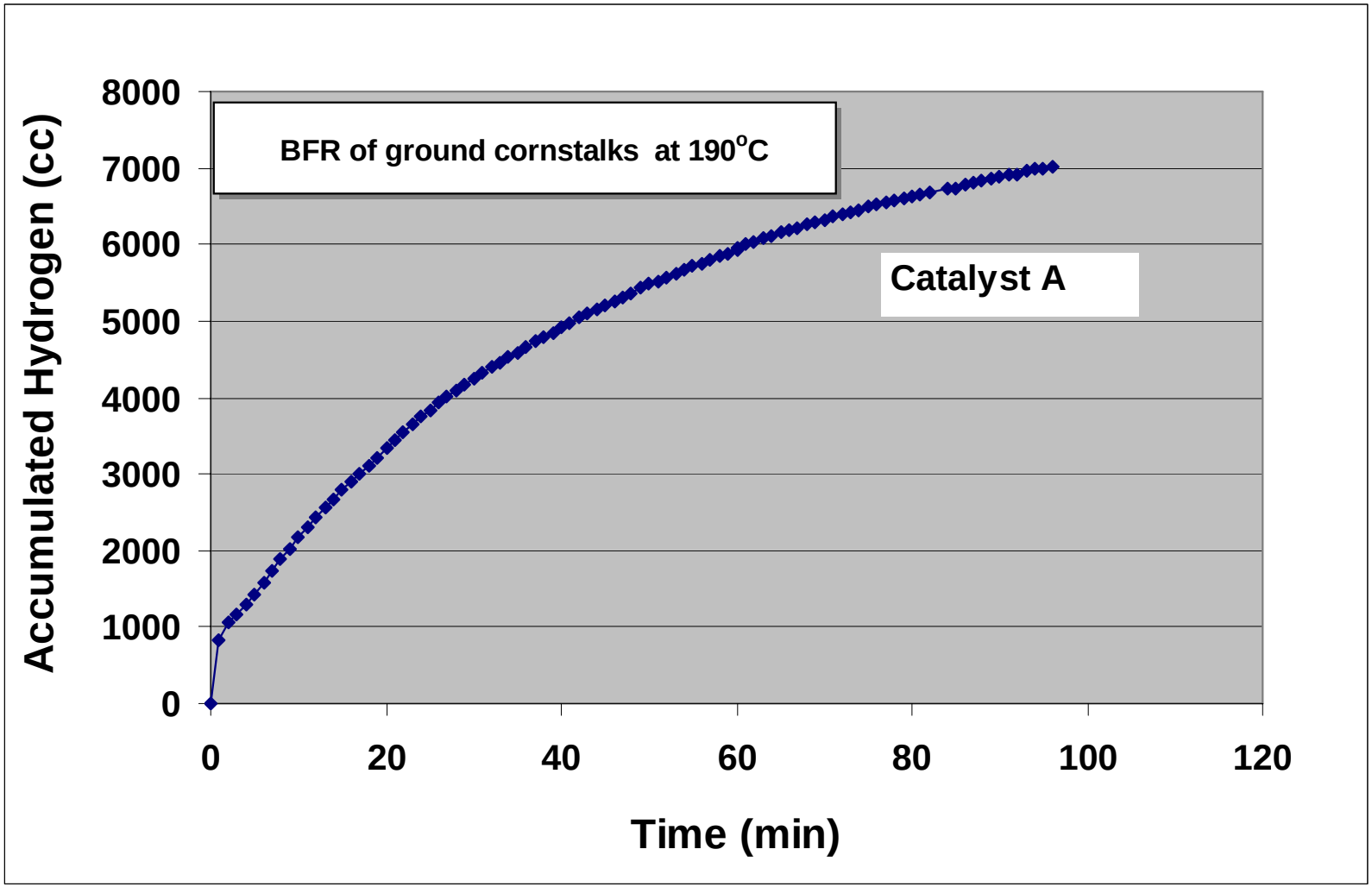
Base-Facilitated Reformation of Corn Kernels - Batch Reactor



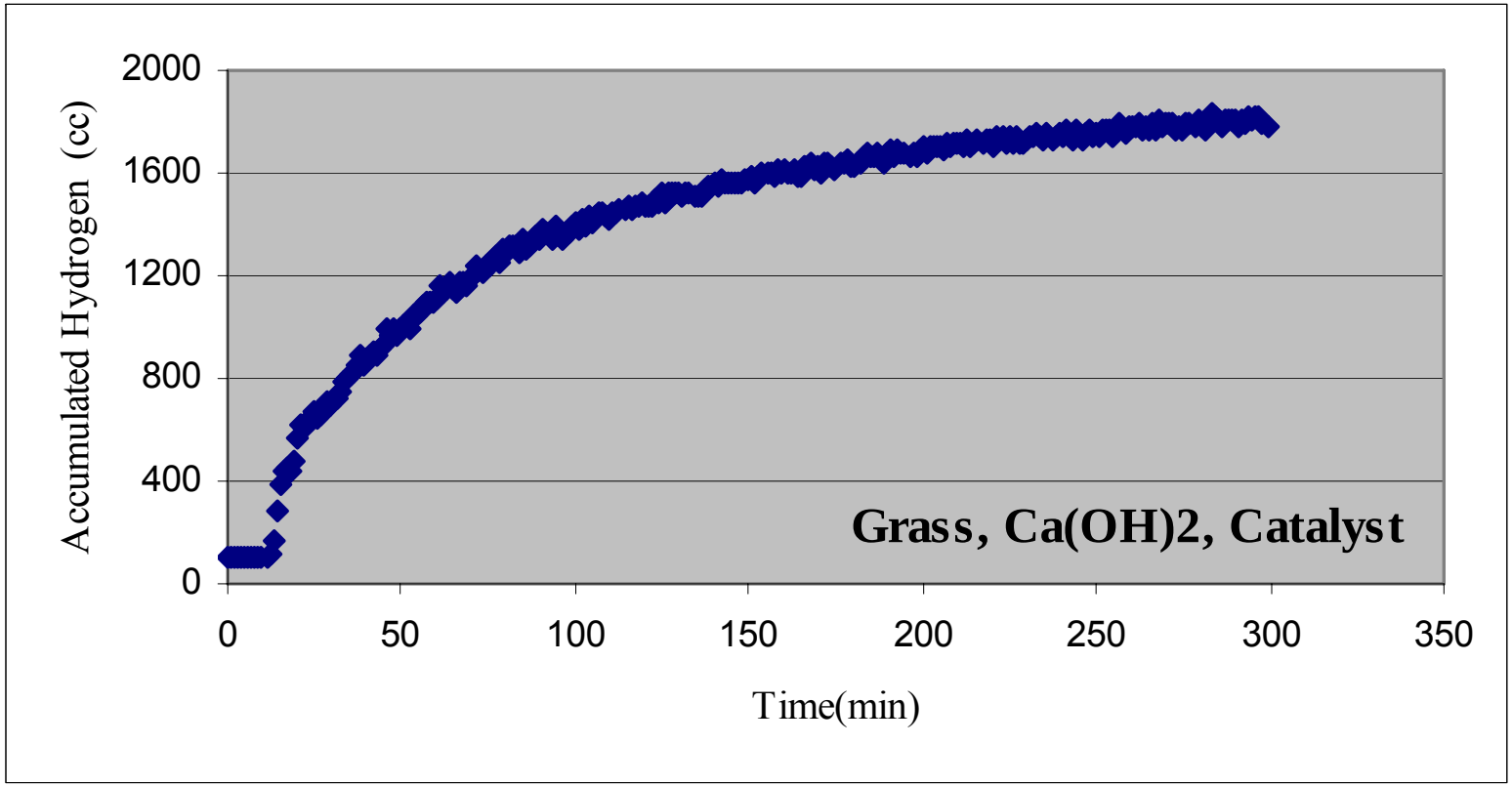
Base-Facilitated Reforming of wood (Batch Reactor)



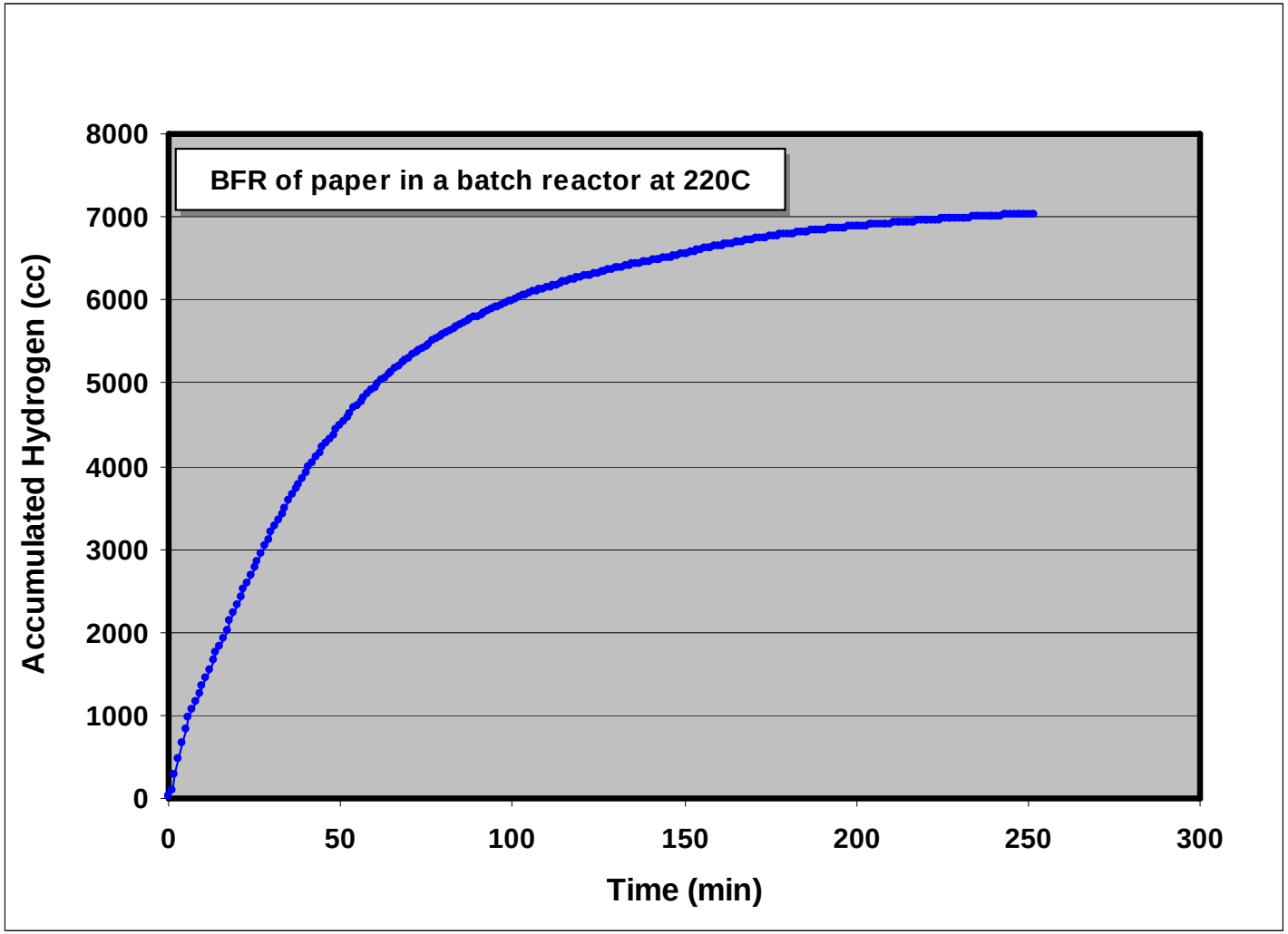
Base-Facilitated Reforming of Cornstalks (Batch Reactor)



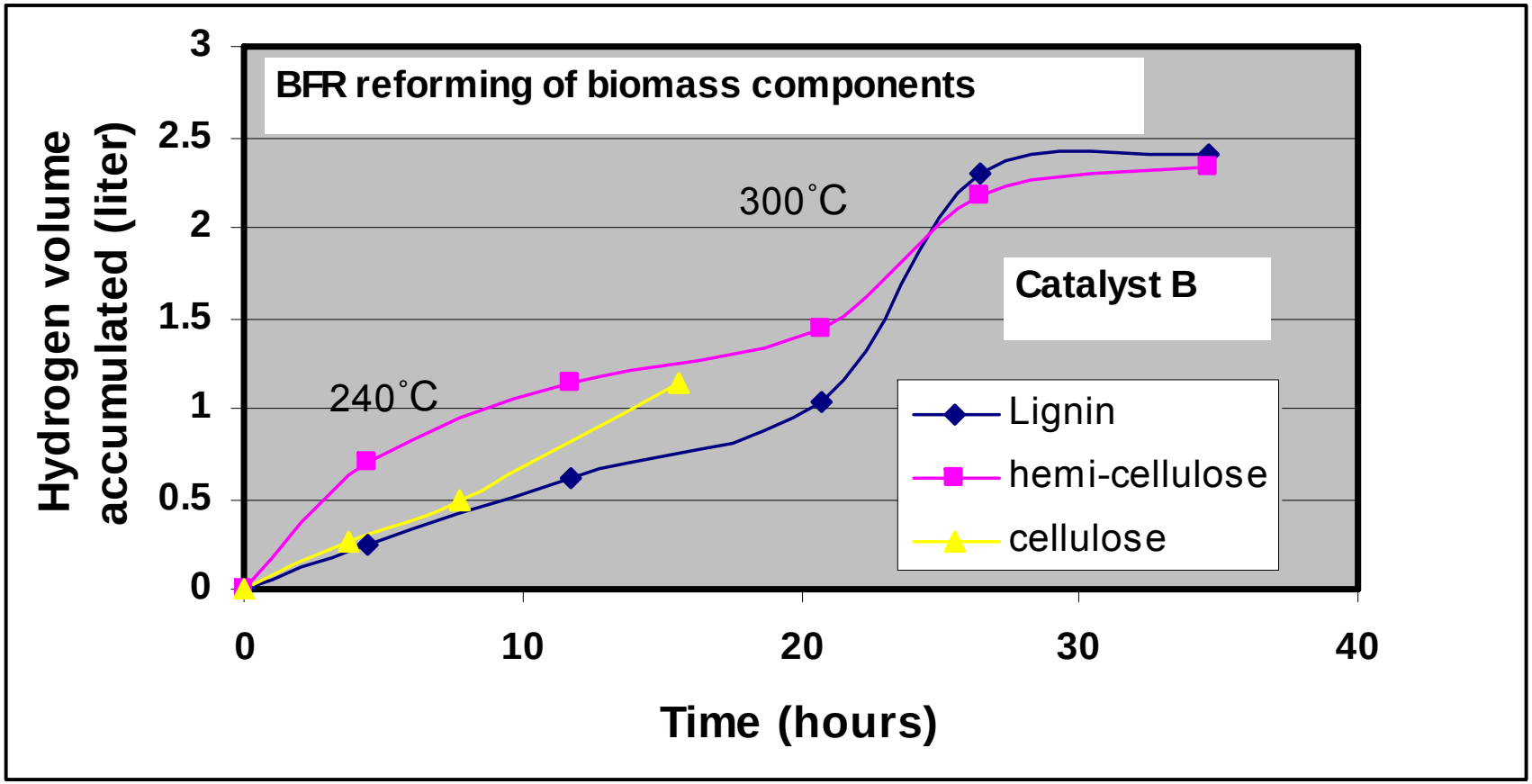
Base-Facilitated Reformation of Grass (300˚C)- Batch Reactor



Base-Facilitated Reforming of Paper (Batch Reactor)



Base-Facilitated Reforming of biomass components (Batch Reactor)



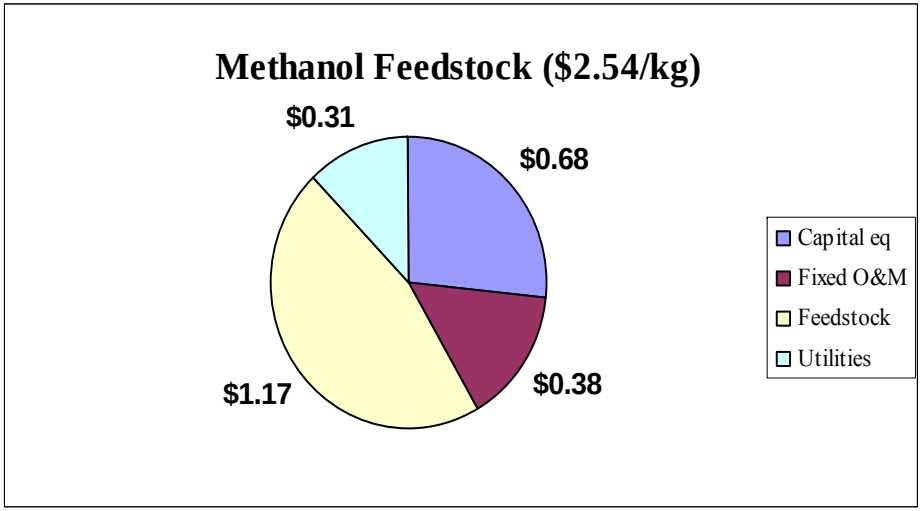
Base-Facilitated Reforming

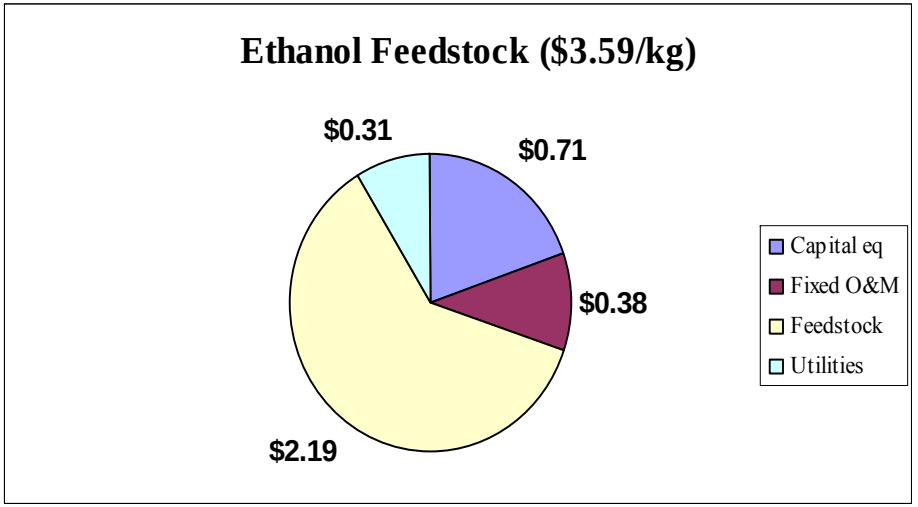
Economics

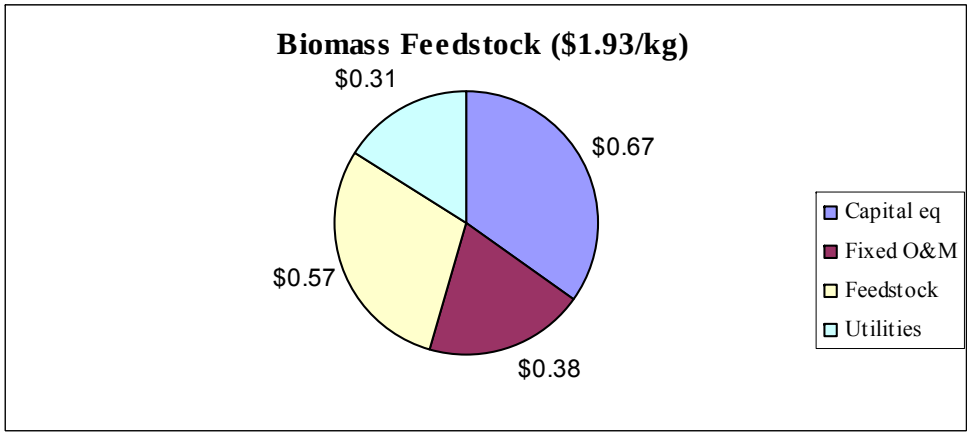
Economics of Base-Facilitated Reformation

- Used DOE H2A economic analysis tool
  - 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

Reformation at 1,500 kg H_2 Per Day
Cost Structure







Base-Facilitated Reformation (BFR)

- Work toward commercialization

Reactors For Base-Facilitated Reforming

Batch

Lab batch reactor 100 ml open volume (rate: 3L H_2/hr for 0.5hrs)

Semi-Continuous

Semi-Continuous reactor with storage tank 4L open volume (rate: 10L H_2/hr for 8 hrs)

Continuous

Continuous reactor producing H_2 (rate: 100L/hr as long as needed)

Prototype 10 kg H_2/day Base-Facilitated Solid Biomass Fluidized Bed Reactor

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By-Product (carbonate) Recycling

What do we do with solid carbonate?

- Dispose the carbonate to sequester CO_2
- Use the carbonate to generate pure CO_2 for various industrial applications (soda, liquid fuel synthesis etc..)
- Sell Na_2CO_3 or $CaCO_3$ for various industrial applications (i.e. glass)
- Recycling back to hydroxide

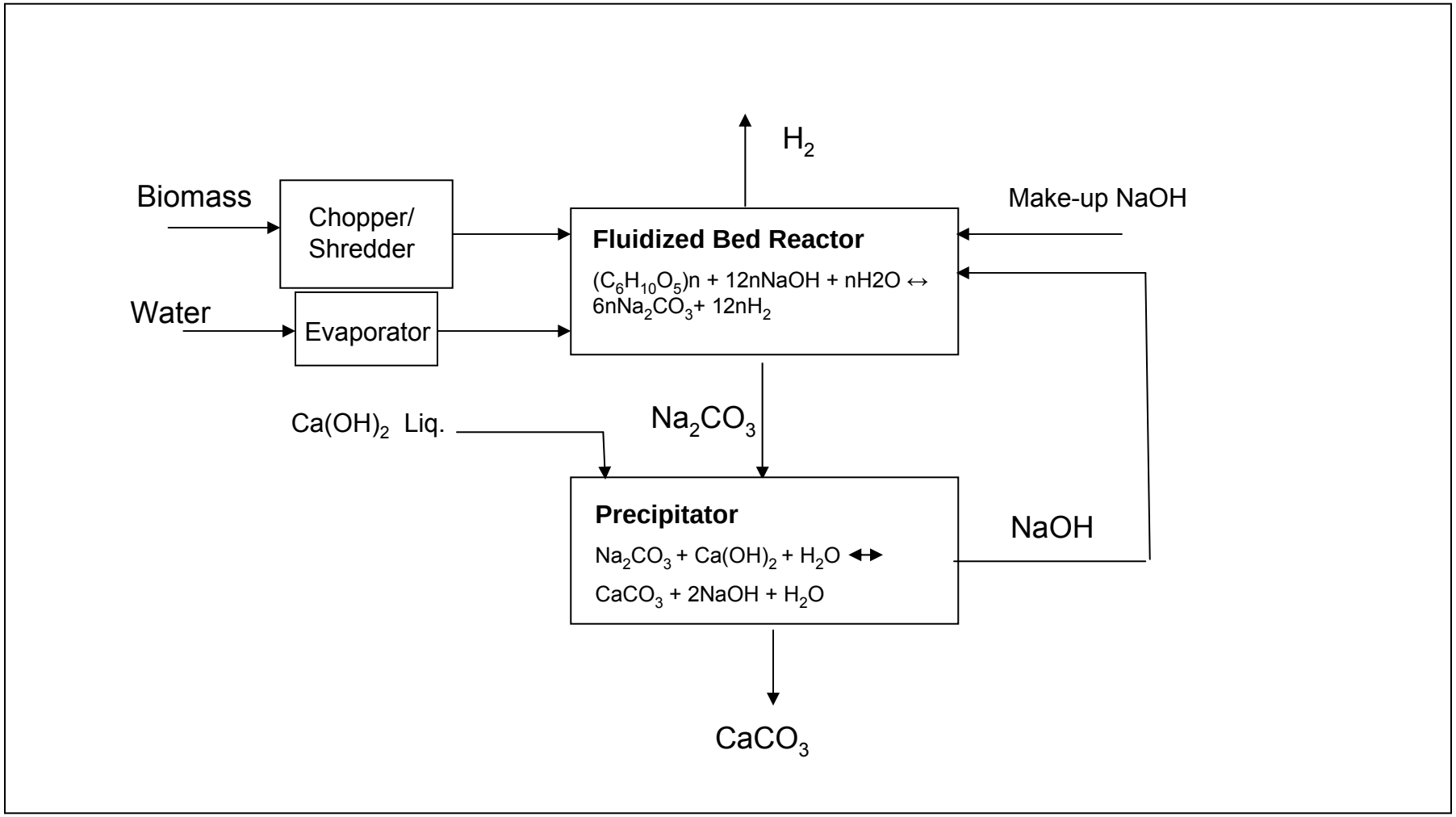
Recycling of Na_2CO_3

- $Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$
- $CaCO_3 \xrightarrow{heat} CaO + CO_2$
- $CaO + H_2O \rightarrow Ca(OH)_2$

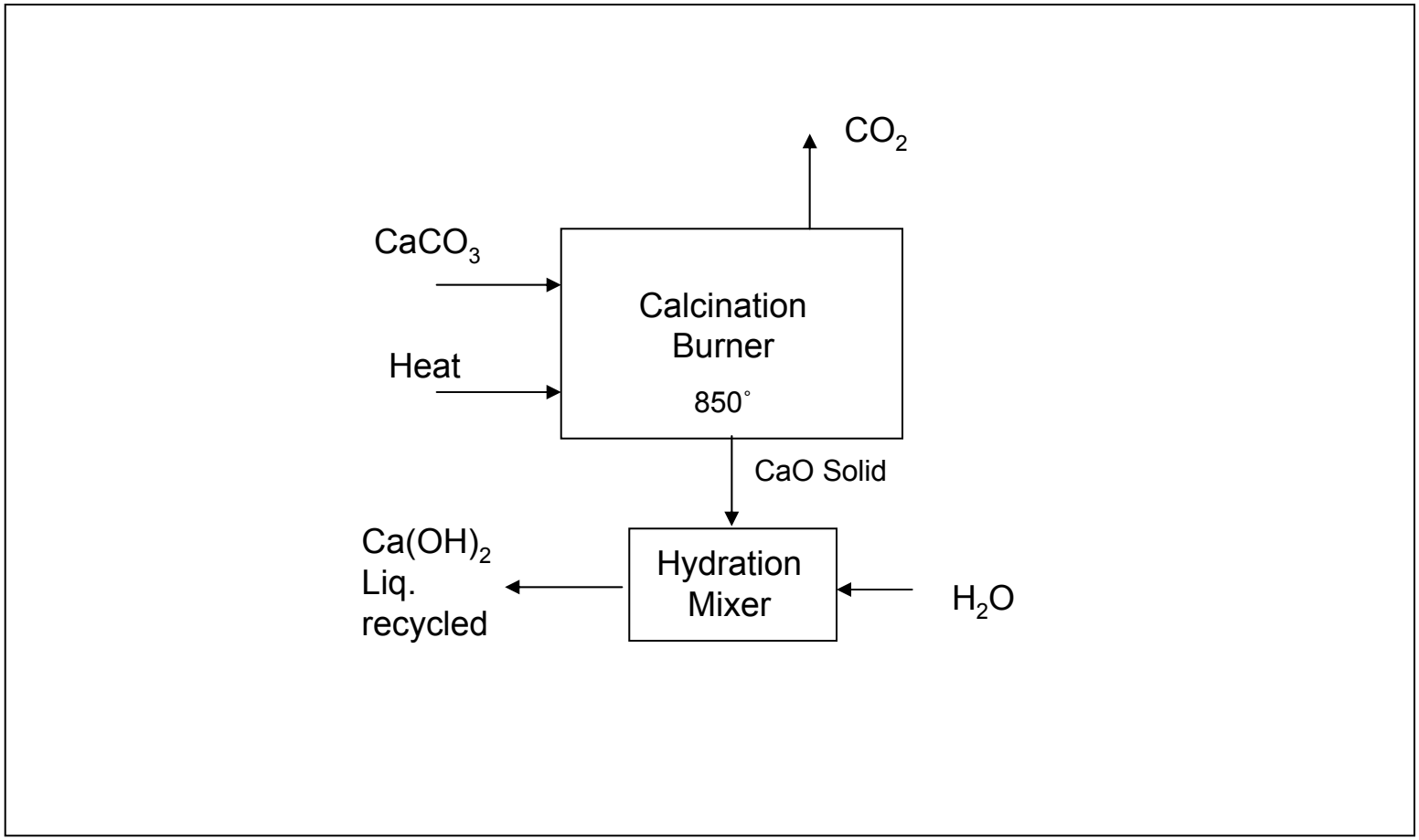
Common commercial process (Recausticizing) in paper mill industry

Base-Facilitated Reformation

Flow Diagram of Biomass (solid) BFR Process



Base-Facilitated Reformation
Flow Schematic of Recycling Process



Summary

- The Base-Facilitated Reforming (BFR) process has been demonstrated on wide variety of fuels. A biomass reforming process towards commercialization is under development
- The reforming temperatures using the BFR process are significantly lower than the steam reformation process of the fuels
- Reformation in a liquid phase at low temperatures of some fuels was demonstrated.
- The BFR process exhibits good rates at the low temperatures of operation.
- The BFR process is a simple one step process. Pure H_2 and no CO and CO_2 produced. WGS reaction and PSA are therefore avoided and the process is environmentally clean
- The BFR process is economically feasible and competes well with other technologies

Summary

- Base-facilitated reforming (BFR) process has been demonstrated on wide variety of fuels.
- High conversion of raw biomass feedstocks and high yield (close to 100%) of H_2 was obtained using BFR.
- The process operates at low temperatures (<300˚) without CO and CO_2 gases and it is economically feasible.
- Developmental work towards commercialization is underway.

Progress in Development and Commercialization of Base-Facilitated Reforming Technology

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