Supplementary Material:

Millisecond Autothermal Steam Reforming of Cellulose for Synthetic Biofuels by Reactive Flash Volatilization

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The supplementary material contains a description of the assumptions that went into the construction of figure 7.

Construction of Figure 7

The development of Figure 7 required the review of several gasification publications and the selection of processing parameters with the goal of comparing several technologies. Due to the heterogeneous feed used in gasification, the two operating criteria selected for comparison were the carbon mass velocity and the carbon space velocity.

The molar flow rate of carbon has been selected as the processing parameter for comparison for several reasons. The heterogeneous feedstock (air/oxygen and solid material such as biomass) of most gasifiers permits a wide range of total mass feed rate depending on parameters such as the C/O ratio of the solid, the S/C ratio of the gasifier feed, and equivalence ratio of the gasifier. However, the molar flow rate of atomic carbon is the common parameter to which many of these factors are related.

The carbon mass velocity (CMV) has been defined,

$$CMV = \frac{Mass\ Flow\ C}{Mass\ Catalyst} \qquad \text{(S1).}$$

The carbon space velocity (CSV) has been defined,

$$CSV = \frac{Molar\ Flow\ C}{Reaction\ Volume} \qquad \text{(S2).}$$

The “reaction volume" is considered to be the volume necessary to complete the reaction chemistry for the conversion of biomass/cellulose to synthesis gas. Because the strict definition varies by reactor type, the reaction volume will be carefully defined for each technology.

The considered technologies include 1.) fluidized bed gasifiers followed by catalytic tar cleaning, 2.) integrated catalytic fluidized beds, 3.) fluidized bed fast pyrolysis reactors and steam reforming of fast pyrolysis oils to synthesis gas, and 4.) reactive flash volatilization of cellulose.

Each of these technologies can be operated over a wide range of process parameters. Therefore, experimental trials were selected from publications that both exhibited optimal performance (low selectivity to tars) and high throughput.

Technologies that require two separate reactors (sets 1 and 3) were reported from one publication if possible. Additionally, multiple catalytic metals including dolomite, rhodium, nickel, and ruthenium were considered, because these catalysts were well-represented in the gasification literature.

Figure S1 and Figure 7 show the results of considering the process parameters for all of these considered technologies grouped by type.

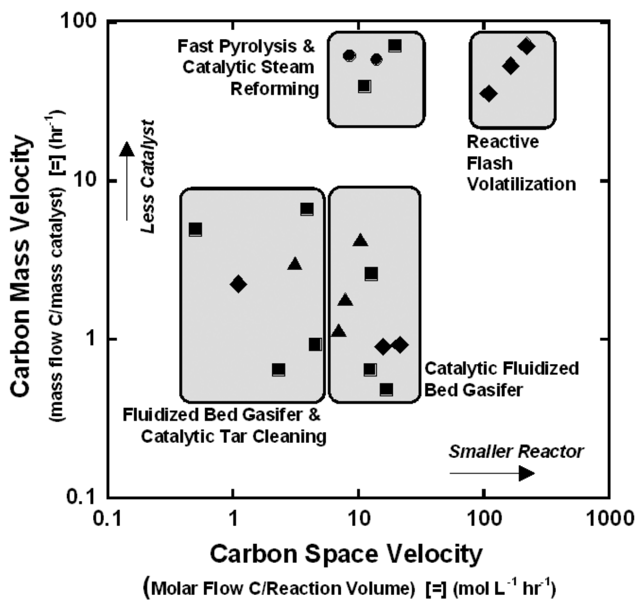

Figure S1. Various processes to convert organic solids to synthesis gas exhibit operational performance grouped by process type despite utilizing several different catalysts: Dolomite (▲), Ni (■), Rh (◆), Ru (●). The carbon space velocity provides a measure of the reactor volume by relating the molar processing of carbon to the volume necessary for chemical conversion. The carbon mass velocity provides a measure of catalyst usage by relating the molar processing of carbon to the mass of the catalyst.

A. Data and Information for Fluidized Bed Gasifiers and Catalytic Tar Cleaning

Table S1. Tabulated process parameters for fludized bed gasifiers and catalytic tar cleaning.

Publication	[10]	[15,18]	[8]	[16]	[17]	[19]
Feed Solid Material (g/hr)	9	3.6	840	450	470	5000
Flow Carbon (g/hr)	4.139	1.683	422.52	193.5	177.3	2300
Flow Carbon (mole/hr)	0.345	0.140	35.2100	16.125	14.78	191.7
Catalyst Type	Rh	Ni	Ni	NiO-Mg	Dolomite / Ni	Dolomite
All catalyst loading (g)	1.837	0.34	650	29	190.0	752
Reaction Volume (mL)	300	300	15260	4116	3313	61700
Temperature (deg C)	650	650	750	780	700	840
Gasifiying Medium	Oxygen	Oxygen	Steam	Steam	Steam / O_2	Steam / O_2
Carbon Space Velocity (mole/hr L)	1.1	0.5	2.3	3.9	4.5	3.1
Carbon Mass Velocity (hr^{-1})	2.253	4.951	0.650	6.673	0.933	3.059

The solid material for all cases was either wood or microcrystalline cellulose. The flow of carbon was determined based on the feedstock analysis of each publication. The total mass of catalyst loading does not include supports such as alumina or silica. The reaction volume for this technology was the sum of the gasifier total volume and the volume occupied by the tar cleaning catalyst (including void space between catalyst particles).

B. Data and Information for Catalytic Fluidized Bed Gasifiers

Table S2. Tabulated process parameters for catalytic fludized bed gasifiers.

Publication	[2,3]	[4]	[5]	[8]	[15]	[11]	[12]	[13]
Feed Solid Material (g/hr)	18.6	5.1	3.6	840	10.76	602	10550	9400
Flow Carbon (g/hr)	8.923	2.264	1.656	422.52	5.19	308.6	5275	4700
Flow Carbon (mole/hr)	0.7436	0.1887	0.1380	35.21	0.433	25.71	439.6	391.7
Catalyst Type	Ni	Rh	Rh	Ni	Ni-Mg	Dolomite	Dolomite	Dolomite
All catalyst loading (g)	18.23	2.437	1.837	650	2.0	72	2940	4100
Reaction Volume (cc)	44.5	8.84	8.84	2867	34.39	2490	56500	56500
Temperture (deg C)	700	650	700	750	700	800	816	834
Gasifiying Medium	Steam	Oxygen	Oxygen	Steam	Steam	Oxygen	Oxygen	Oxygen
Carbon Space Velocity (mole/hr L)	16.7	21.3	15.6	12.3	12.6	10.3	7.8	6.9
Carbon Mass Velocity (hr^{-1})	0.489	0.929	0.901	0.65	2.597	4.286	1.794	1.146

The solid material for all cases was either wood or microcrystalline cellulose. The flow of carbon was determined based on the feedstock analysis of each publication. The total mass of catalyst loading does not include supports such as alumina or silica. The reaction volume for catalytic fluidized bed gasifiers was defined as the volume occupied by the catalyst but does not include reactor volume not occupied by the catalyst such as freeboard.

C. Data and Information for Fast Pyrolysis and Catalytic Steam Reforming

Table S3. Tabulated process parameters for fast pyrolysis and catalytic steam reforming.

Publication	[20,21]	[3,22]	[3,21]	[20,22]
Feed Solid Material (g/hr)	1970	15	15	1970
Flow Carbon (g/hr)	888.6	5.805	5.805	888.6
Flow Carbon (mole/hr)	74.05	0.484	0.4840	74.05
Catalyst Type	Ni	Ru	Ru	Ru
All catalyst loading (g)	12.44	0.094	0.146	15.3
Reaction Volume (mL)	3770	56.98	43.5	5350
Temperature (deg C)	825	800	800	825
Gasifiying Medium	Steam	Steam	Steam	Steam
Carbon Space Velocity (mole/hr L)	19.6	8.5	11.1	13.8
Carbon Mass Velocity (hr^{-1})	71.43	61.56	39.76	58.07

The solid material for all cases was either wood or microcrystalline cellulose. The two separate reactors in each publication was scaled by the mass flow rate. The flow of carbon was determined based on the feedstock analysis of each publication. The total mass of catalyst loading does not include supports such as alumina or silica. The reaction volume for fast pyrolysis and catalytic steam reforming was defined as the sum of the volume occupied by the fast pyrolysis reactor tube and the volume occupied by the steam reforming catalyst (including void space between catalyst particles).

D. Data and Information for Reactive Flash Volatilization

Table S3. Tabulated process parameters for fast pyrolysis and catalytic steam reforming.

Publication	[1]	[1]	[1]
Feed Solid Material (g/hr)	30	40	20
Flow Carbon (g/hr)	13.32	17.76	8.88
Flow Carbon (mole/hr)	1.11	1.48	0.7400
Catalyst Type	Rh	Rh	Rh
All catalyst loading (g)	0.25	0.25	0.25
Reaction Volume (mL)	6.81	6.81	6.81
Temperature (deg C)	833	850	750
Gasifiying Medium	Oxygen	Oxygen	Oxygen
Carbon Space Velocity (mole/hr L)	163	217	108.7
Carbon Mass Velocity (hr^{-1})	53.28	71.04	35.52

The solid material for all cases was microcrystalline cellulose. The total mass of catalyst loading does not include the support alumina. The reaction volume for reactive flash volatilization reactor was defined as the volume occupied by the catalyst (including void space between catalyst particles) but does not include reactor volume not occupied by the catalyst above and below the fixed bed.

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