Optimization of hydrogen production from pyrolysis of biomass waste

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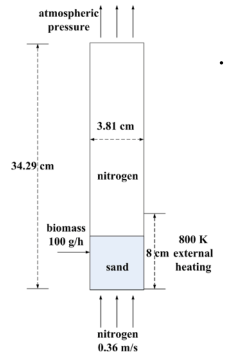
- ***We developed an CFD aided ML-based tool for rapid assessment and optimization of different compositions of biomass in a fluidized bed reactor. First, we use CFD to simulate fluidized bed reactors with known inlet biomass mixtures and obtain corresponding syngas yields. A lumped kinetic mechanisms represents the conversion of Cellulose, Hemicellulose, and Lignin, as well as subsequent cracking of tars into non-condensable gases (H2, CO, CO2, CH4). We use Bayesian analysis/optimization to obtain the ideal operational and mass flow conditions for hydrogen production.***

Challenges

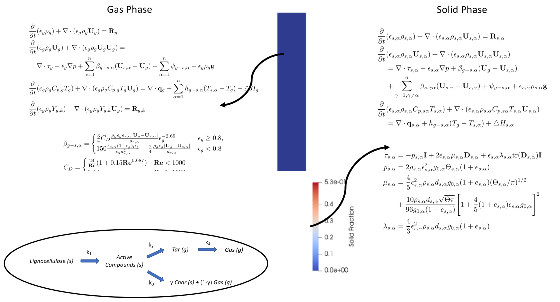
- ***Syngas yields depend on feedstock composition. The operation and performance of the pyrolysis system depend entirely on the operating temperature, and feedstock composition.***
- ***Rapid assessment tools are needed to assess optimization routes depending on the characteristics of the feedstock.***

System Description



- ***The experimental data used for model validation is taken from Xiong et al. [1]. In these experiments, a laboratory-scale fluidized bed reactor with 0.34 m in height and 0.038 m in diameter is operated in the bubbling fluidization regime. Biomass with density of 400 kg/m3 and approximate diameter ranges of 2.5x10-4 m to 4x10-4 m, is fed from a side injector at a rate of 0.1 kg/h, while nitrogen as fluidization gas is added through the bottom at a speed of 0.36 m/s. The temperature of the reactor walls and fluidization nitrogen is set to 773 K***

Modeling and simulation



Gas Phase

$$\frac{\partial}{\partial t}(\epsilon_g\rho_g)+\nabla\cdot(\epsilon_g\rho_g\mathbf{U}_g)=\mathbf{R}_g$$

$$\frac{\partial}{\partial t}(\epsilon_g\rho_g\mathbf{U}_g)+\nabla\cdot(\epsilon_g\rho_g\mathbf{U}_g\mathbf{U}_g)=$$

$$\nabla\cdot\tau_g-\epsilon_g\nabla p+\sum_{\alpha=1}^{n}\beta_{g-s,\alpha}(\mathbf{U}_{s,\alpha}-\mathbf{U}_g)+\sum_{\alpha=1}^{n}\psi_{g-s,\alpha}+\epsilon_g\rho_g\mathbf{g}$$

$$\frac{\partial}{\partial t}(\epsilon_g\rho_g C_{p,g}T_g)+\nabla\cdot(\epsilon_g\rho_g C_{p,g}T_g\mathbf{U}_g)=\nabla\cdot\mathbf{q}_g+\sum_{\alpha=1}^{n}h_{g-s,\alpha}(T_{s,\alpha}-T_g)+\triangle H_g$$

$$\frac{\partial}{\partial t}(\epsilon_g\rho_g Y_{g,k})+\nabla\cdot(\epsilon_g\rho_g Y_{g,k}\mathbf{U}_g)=\mathbf{R}_{g,k}$$

$$\beta_{g-s,\alpha}=\begin{cases}\frac{3}{4}C_D\frac{\rho_g\epsilon_g\epsilon_{s,\alpha}|\mathbf{U}_g-\mathbf{U}_{s,\alpha}|}{d_{s,\alpha}}\epsilon_g^{-2.65} & \epsilon_g\geq 0.8,\\ 150\frac{\epsilon_{s,\alpha}(1-\epsilon_g)\mu_g}{\epsilon_g d_{s,\alpha}^2}+\frac{7}{4}\frac{\rho_g\epsilon_g|\mathbf{U}_g-\mathbf{U}_{s,\alpha}|}{d_{s,\alpha}} & \epsilon_g<0.8\end{cases}$$

$$C_D=\begin{cases}\frac{24}{\mathbf{Re}}(1+0.15\mathbf{Re}^{0.687}) & \mathbf{Re}<1000\end{cases}$$

Solid Phase

$$\frac{\partial}{\partial t}(\epsilon_{s,\alpha}\rho_{s,\alpha})+\nabla\cdot(\epsilon_{s,\alpha}\rho_{s,\alpha}\mathbf{U}_{s,\alpha})=\mathbf{R}_{s,\alpha}$$

$$\frac{\partial}{\partial t}(\epsilon_{s,\alpha}\rho_{s,\alpha}\mathbf{U}_{s,\alpha})+\nabla\cdot(\epsilon_{s,\alpha}\rho_{s,\alpha}\mathbf{U}_{s,\alpha}\mathbf{U}_{s,\alpha})$$

$$=\nabla\cdot\tau_{s,\alpha}-\epsilon_{s,\alpha}\nabla p+\beta_{g-s,\alpha}(\mathbf{U}_g-\mathbf{U}_{s,\alpha})$$

$$+\sum_{\gamma=1,\gamma\neq\alpha}^{n}\beta_{s,\gamma\alpha}(\mathbf{U}_{s,\gamma}-\mathbf{U}_{s,\alpha})+\psi_{g-s,\alpha}+\epsilon_{s,\alpha}\rho_{s,\alpha}\mathbf{g}$$

$$\frac{\partial}{\partial t}(\epsilon_{s,\alpha}\rho_{s,\alpha}C_{p,s\alpha}T_{s,\alpha})+\nabla\cdot(\epsilon_{s,\alpha}\rho_{s,\alpha}C_{p,s\alpha}T_{s,\alpha}\mathbf{U}_{s,\alpha})$$

$$=\nabla\cdot\mathbf{q}_{s,\alpha}+h_{g-s,\alpha}(T_g-T_{s,\alpha})+\triangle H_{s,\alpha}$$

$$\tau_{s,\alpha}=-p_{s,\alpha}\mathbf{I}+2\epsilon_{s,\alpha}\mu_{s,\alpha}\mathbf{D}_{s,\alpha}+\epsilon_{s,\alpha}\lambda_{s,\alpha}\mathrm{tr}(\mathbf{D}_{s,\alpha})\mathbf{I}$$

$$p_{s,\alpha}=2\rho_{s,\alpha}\epsilon_{s,\alpha}^2 g_{0,\alpha}\Theta_{s,\alpha}(1+e_{s,\alpha})$$

$$\mu_{s,\alpha}=\frac{4}{5}\epsilon_{s,\alpha}^2\rho_{s,\alpha}d_{s,\alpha}g_{0,\alpha}(1+e_{s,\alpha})(\Theta_{s,\alpha}/\pi)^{1/2}$$

$$+\frac{10\rho_{s,\alpha}d_{s,\alpha}\sqrt{\Theta\pi}}{96g_{0,\alpha}(1+e_{s,\alpha})}\left[1+\frac{4}{5}(1+e_{s,\alpha})\epsilon_{s,\alpha}g_{0,\alpha}\right]^2$$

$$\lambda_{s,\alpha}=\frac{4}{3}\epsilon_{s,\alpha}^2\rho_{s,\alpha}d_{s,\alpha}g_{0,\alpha}(1+e_{s,\alpha})$$

A multi-fluid model is selected to model the dynamics of the gas-solid interaction while multi-component, multi-step kinetics are selected to represent the kinetics of biomass pyrolysis. The model was solved using the solvers for the open-source CFD software OpenFOAM-v9 in which the phases are considered as an interpenetrating continuum with mass, momentum, and energy interactions. Three different phases are considered in the modeling framework: a gas phase that describes the gaseous products of the reaction as well as the inert carrier gas, a particle phase that describe the biomass reacting particles, and a bed phase that describe the solid fluidization medium. The three major components of biomass are cellulose, hemicellulose and lignin. Miller-Bellan [2] proposed a decomposition mechanism that describe the reaction kinetics of the 3 major components of biomass. In this mechanism, each major biomass component undergoes first order reactions that result in different composition of bio-tar, non-condensable gases, and bio-char. Each component has its own temperature-dependent reaction rate represented by Arrhenius-like expressions for first order kinetics.

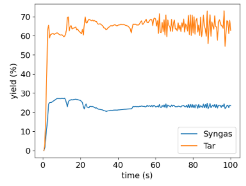
Type	Reaction	Pre-exponential factor A_i (s^{-1})	Activation Energy E_i $(MJkmol^{-1})$	Char formation ratio y_i
Cellulose	$\mathrm{Cell}\xrightarrow{k_{c,1}}\mathrm{Acell}$	2.8e9	242.4	–
	$\mathrm{Acell}\xrightarrow{k_{c,2}}\mathrm{Tar}$	3.28e14	196.5	–
	$\mathrm{Acell}\xrightarrow{k_{c,3}}y\,\mathrm{Char}+(1-y)\,\mathrm{Gas}$	1.3e10	150.5	0.35
Hemicellulose	$\mathrm{Hemi}\xrightarrow{k_{h,1}}\mathrm{Ahemi}$	2.1e16	186.7	–
	$\mathrm{Ahemi}\xrightarrow{k_{h,2}}\mathrm{Tar}$	8.75e15	202.4	–
	$\mathrm{Acell}\xrightarrow{k_{h,3}}y\,\mathrm{Char}+(1-y)\,\mathrm{Gas}$	2.6e11	145.7	0.60
Lignin	$\mathrm{Lig}\xrightarrow{k_{l,1}}\mathrm{Alig}$	9.6e8	107.6	–
	$\mathrm{Alig}\xrightarrow{k_{l,2}}\mathrm{Tar}$	1.5e9	143.8	–
	$\mathrm{Alig}\xrightarrow{k_{l,3}}y\,\mathrm{Char}+(1-y)\,\mathrm{Gas}$	7.7e6	111.4	0.75
Tar	$\mathrm{Tar}\xrightarrow{k_{tar}}\mathrm{Gas}(\mathrm{CO_2},\mathrm{CO},\mathrm{H_2},\mathrm{CH_4})$	4.25e6	108	–
Heterogeneous reactions	$\mathrm{C}+\mathrm{CO_2}\xrightarrow{kt_{CO_2}}2\,\mathrm{CO}$	2.68e4	589	–
	$\mathrm{C}+\mathrm{H_2O}\xrightarrow{kt_{H_2O}}\mathrm{CO}+\mathrm{H_2}$	2.68e4	589	–
	$\mathrm{C}+2\,\mathrm{H_2}\xrightarrow{kt_{H_2}}\mathrm{CH_4}$	2.68e4	0.589	–
Homogeneous reactions	$\mathrm{CO}+\mathrm{H_2O}\xrightarrow{kh_{CO}}\mathrm{CO_2}+\mathrm{H_2}$	1.51e3	2.780	–
	$\mathrm{CH_4}+\mathrm{H_2O}\xrightarrow{kh_{CH_4}}\mathrm{CO}+3\,\mathrm{H_2}$	3.0e8	–	–

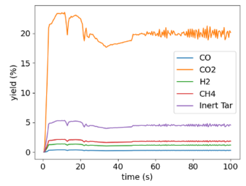
Validation

The feedstock mass fraction compositions fed to the experimental reactor were:

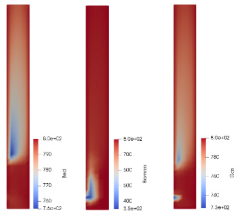
- ***Cellulose: 0.41***
- ***Hemicellulose: 0.32***
- ***Lignin: 0.27***

Characterization of biomass in terms of its cellulose, hemicellulose and lignin content, allows for generalizations regardless of the specific biomass feedstocks. This means that the differences between pinewood and switchgrass can be accounted by their lignocellulosic content.





Temperature Profiles



	Syngas	Tar	Temperature
Experiment	71.7	22.3	773 K
Simulation	67.1	23.4	786 K

Optimization

Bayesian optimization is a powerful technique for optimizing expensive objective functions. CFD evaluations can rapidly become very expensive with demands on resolution and accuracy. Probabilistic regression models are usually used to approximate expensive function evaluations. These models (M) are initialized using a small set of samples from the domain (X) . Following this initialization phase, new locations within the domain are sequentially selected by optimizing an acquisition function (S) which uses the current model as a cheap surrogate for the expensive objective function (f)

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Algorithm 1 Sequential Model-Based Optimization
  Input: $f, \mathcal{X}, S, \mathcal{M}$
  $\mathcal{D} \leftarrow \textsc{InitSamples}(f, \mathcal{X})$
  for $i \leftarrow |\mathcal{D}|$ to $T$ do
    $p(y \mid \mathbf{x}, \mathcal{D}) \leftarrow \textsc{FitModel}(\mathcal{M}, \mathcal{D})$
    $\mathbf{x}_i \leftarrow \arg\max_{\mathbf{x}\in\mathcal{X}} S(\mathbf{x},\ p(y \mid \mathbf{x}, \mathcal{D}))$
    $y_i \leftarrow f(\mathbf{x}_i)$    ▷ Expensive step
    $\mathcal{D} \leftarrow \mathcal{D} \cup (\mathbf{x}_i, y_i)$
  end for
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The problem statement can be summarized as:

$$\min_{\mathbf{x}} \quad y(\mathbf{x})$$
$$\text{s.t.} \quad g(\mathbf{x}) \geq 1-\xi$$

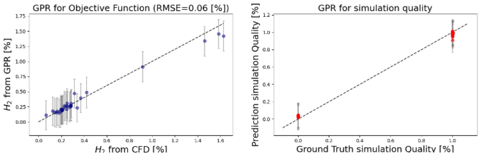
where:
y → Hydrogen yield
x → Temperature
water content
mass flow rate
lignocellulosic fraction

An initial random design is proposed parametrized by a set of input parameters that affect the outputs of the system. 40 simulations are initially proposed varying the parameters randomly over the parameter space.

Parameters	Ranges
Temperature (T, [K])	(600 – 1000)
Biomass Moisture (H2O, [-])	(0.01 – 0.15)
Mass flow rate (FR, [kg/s])	(2.8e-5 – 1.9e-4)
Cellulose content (Cell [-])	(0 – 0.9)
Hemicellulose content (Hcell, [-])	(0 – 0.9)
Lignin content (Lig, [-])	(0 – 0.9)

Cases	T (K)	H2O (mass frac)	FR (kg/s)	cell (mass frac)	hcell (mass frac)	lig (mass frac)	Fail
Case_0	915	0.14475	0.000062425	0.50625	0.372164063	0.121585938	1
Case_1	685	0.13775	0.000123175	0.03375	0.619607813	0.346642188	1
Case_2	715	0.13075	0.000082675	0.57375	0.100701563	0.325548438	1
Case_3	935	0.03625	0.000058375	0.73125	0.015117188	0.253632813	0
Case_4	635	0.07475	0.000066475	0.86625	0.043635937	0.090114062	1
Case_5	845	0.12375	0.000094825	0.64125	0.012107813	0.346642188	0
Case_6	655	0.10275	0.000046225	0.32625	0.447201563	0.226548438	1
Case_7	895	0.08175	0.000111025	0.19125	0.300248438	0.508501563	0
Case_8	605	0.08875	0.000131275	0.77625	0.017620313	0.206129688	1
Case_9	825	0.01875	0.000115075	0.46125	0.369717188	0.169032813	1
Case_10	695	0.05725	0.000054325	0.84375	0.072070313	0.084179688	1
Case_11	625	0.06425	0.000167725	0.55125	0.378632813	0.070117188	1
Case_12	875	0.12725	0.000127225	0.28125	0.428554688	0.290195313	1
Case_13	855	0.11325	0.000183925	0.16875	0.252492188	0.578757813	1
Case_14	745	0.03275	0.000090775	0.88875	0.098873438	0.012376563	1
Case_15	765	0.10975	0.000086725	0.07875	0.155460938	0.765789063	1
Case_16	905	0.11675	0.000179875	0.75375	0.119123438	0.127126563	0
Case_17	665	0.06075	0.000034075	0.70875	0.114679688	0.176570313	1
Case_18	705	0.08525	0.000102925	0.01125	0.856504688	0.132245313	1
Case_19	865	0.02225	0.000098875	0.25875	0.108407813	0.632842188	0
Case_20	785	0.02925	0.000119125	0.05625	0.775054688	0.168695313	1
Case_21	775	0.09575	0.000147475	0.79875	0.142635938	0.058614063	1
Case_22	885	0.04675	0.000159625	0.66375	0.170226563	0.166023438	0
Case_23	955	0.13425	0.000050275	0.12375	0.187298438	0.688951563	1
Case_24	835	0.14825	0.000187975	0.82125	0.074404687	0.104345313	1
Case_25	735	0.01175	0.000030025	0.37125	0.488067188	0.140682813	1
Case_26	975	0.12025	0.000143425	0.59625	0.049964063	0.353785938	0
Case_27	615	0.09925	0.000175825	0.48375	0.272967188	0.243282813	1
Case_28	985	0.07125	0.000042175	0.52875	0.132539063	0.338710938	1
Case_29	675	0.01525	0.000074575	0.14625	0.086442188	0.767307813	1
Case_30	805	0.07825	0.000163675	0.41625	0.466270313	0.117479688	1
Case_31	925	0.04325	0.000151525	0.68625	0.003529688	0.310220313	1
Case_32	755	0.14125	0.000139375	0.30375	0.509132813	0.187117188	1
Case_33	725	0.05375	0.000070525	0.10125	0.171885938	0.726864063	1
Case_34	945	0.02575	0.000135325	0.23625	0.438201563	0.325548438	0
Case_35	645	0.06775	0.000171775	0.34875	0.402960938	0.248289063	1
Case_36	795	0.10625	0.000155575	0.39375	0.265992188	0.340257813	1
Case_37	965	0.09225	0.000038125	0.21375	0.274204688	0.512045313	1
Case_38	995	0.05025	0.000106975	0.43875	0.309389063	0.251860938	0
Case_39	815	0.03975	0.000078625	0.61875	0.098648438	0.282601563	1

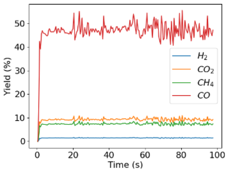
Due to the lumped kinetic limits with the addition of kinetics of syngas cracking, some simulations tend to fail at some input values. We have used Bayesian constrained optimization [3] where we propose constraint functions based on the failed simulations and adapt the optimization to avoid exploration on regions for failing input values.

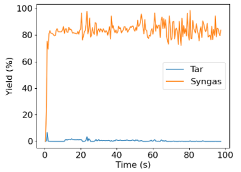


The optimization provides a list of suitable input values, the max of those values and the simulation results with those inputs are:

Input Parameters	Optimal value
Temperature (T, [K])	994.4
Biomass Moisture (H2O, [-])	0.09
Mass flow rate (FR, [kg/s])	1.75E-5
Cellulose content (Cell [-])	0.3269
Hemicellulose content (Hcell, [-])	0.1567
Lignin content (Lig, [-])	0.5278

	Hydrogen Yield (%)
Experimental case	0.35
Optimal sim. case	1.52





Impacts

- ***We have shown that simulation-based optimization can aid process operation by providing realistic optimal operational parameters***
- ***We account for unfeasible parameters by constraining the optimization function based on failed simulations***
- ***This workflow can be extended to many processes were results of the simulation/operation can be used to train the probabilistic model for better predictions.***

[1]. Xiong et, al. Development of a generalized numerical framework for simulating biomass fast pyrolysis in fluidized-bed reactors http://dx.doi.org/10.1016/j.ces.2013.06.017.
[2]. Miller et, al. A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicelluloseand Liqnin Kinetics. https://doi.org/10.1080/00102209708935670.
[3]. Gelbart et, al. Bayesian Optimization with Unknown Constraints. https://doi.org/10.48550/arXiv.1403.5607

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