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DESIGN, FABRICATION, OPERATION AND ASPEN SIMULATION OF OIL SHALE PYROLYSIS AND BIOMASS GASIFICATION PROCESS USING A MOVING BED DOWNDRAFT REACTOR

by

HASSAN GOLPOUR

A DISSERTATION

Presented to the Graduate Faculty of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

2016

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PUBLICATION DISSERTATION OPTION

This dissertation consists of the following four articles, formatted in the style used by the Missouri University of Science and Technology:

Pages 2-20 are intended for submission to the JOURNAL OF UNCONVENTIONAL OIL AND GAS RESOURCES.

Pages 21-45 have been accepted in INTERNATIONAL JOURNAL OF CHEMICAL ENGINEERING.

Pages 46-91 are intended for submission to THE JOURNAL OF BIOMASS AND BIOENERGY.

Pages 92-118 are intended for submission to THE JOURNAL OF RENEWABLE ENERGY.

ABSTRACT

Energy is the major facilitator of the modern life. Every developed and developing economy requires access to advanced sources of energy to support its growth and prosperity. Declining worldwide crude oil reserves and increasing energy needs has focused attention on developing existing unconventional fossil fuels like oil shale and renewable resources such as biomass. Sustainable, renewable and reliable resources of domestically produced biomass comparing to wind and solar energy is a sensible motivation to establish a small-scale power plant using biomass as feed to supply electricity demand and heat for rural development. The work in Paper I focuses on the possibility of water pollution from spent oil shale which should be studied before any significant commercial production is attempted. In Paper II, the proposed Aspen models for oil shale pyrolysis is to identify the key process parameters for the reactor and optimize the rate of production of syncrude from oil shale. The work in Paper III focuses on 1. Design and operation of a vertical downdraft reactor, 2. Establishing an optimum operating methodology and parameters to maximize syngas production through process testing. Finally in Paper IV, a proposed Aspen model for biomass gasification simulates a real biomass gasification system discussed in Paper III.

ACKNOWLEDGEMENTS

First and foremost I would like to express my special appreciation and thanks to my advisor Professor Joseph D. Smith, who has been a tremendous mentor for me. I would like to thank you for encouraging my research and for allowing me to grow as a research scientist. Your advice on both research as well as on my personal life have been priceless. I would also like to thank my committee members, Professor Muthanna H. Al-Dahhan, Professor Douglas K. Ludlow, Professor Gregory Gelles, Professor Ralph E. Flori and Professor Kelly Homan for serving as my committee members even at hardship.

A special thanks to my family. Words cannot express how grateful I am to my mother, father and my brothers for all of the sacrifices that they have made on my behalf. Your prayer for me was what sustained me thus far. I would also like to thank all of my friends who incented me to strive towards my goal, especially Bahar and Peyman which were always there in the moments when there was no one else. I would like to thank the friends I have made while working at the ERDC: Hamid, Jacob, Vivek, Haider, Teja, Anand, Kyle, Prashant, Brian, Uday, Jeremy, Shyam, Jia, and many others. We have worked together, lived together, and in the end we all learned from one another and made good friends.

I dedicate this dissertation to my mother for her constant support and unconditional love.

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1. INTRODUCTION

This work is divided into four papers. Paper 1 discusses the possibility of water pollution due to leachability of heavy metal and metalloids present in processed shale into underground and surface water. Solid to liquid ratio and PH of water was introduced as key factors. Paper 2 investigates the overall simulation of Ex-situ oil shale pyrolysis and contains four blocks in proposed model: 1. Drying zone, 2. Shale oil processing, 3. Natural gas burner and 4. Oil and gas recovery separation. Different cases such as variable temperature, variable feed rate and a combination of both along with variable reactor volume are studied in this section. Paper 3 is the major part of this work and contains design, fabrication and operation of a downdraft biomass gasifier. The reactor is designed to handle high moisture feed stock and is connected to an enclosed combustion chamber to burn the produced syngas. Finally results such as temperature profile inside the reactor and transportation pipe, oxygen concentration, stability of the bed and the quality of syngas flame are given for three types of feed with different moisture content. Paper 4 simulates the gasifier built in paper 3 using Aspen Plus steady state model. Type of feed and air to fuel ratio are introduced as key parameters identifying process yield. Composition and flow rate of produced syngas are defined as process yield which is based on the concentration of H₂ and CO in produced gas stream. Results are given for different air flow rate for each type of feed.

PAPER

I. COMMERCIALIZATION ISSUE OF AN EX-SITU OIL SHALE PROCESS: LECHING STUDIES OF SPENT SHALE

ABSTRACT

During the past decade, significant advancement has been made on various extraction technologies to develop U.S. oil shale resources in an environmentally and economically sustainable fashion. This work has been driven by the increasing demand for domestic transportation fuels and the need to improve U.S. energy security. Although conventional hydrocarbon deposits are becoming more difficult to find and limited in volume, unconventional reserves are relatively easy to locate and plentiful. Hence, development of unconventional resources, particularly shale gas, oil sands, and shale oil continues to receive tremendous attention.

Key mechanical issues that affect online reliability and process efficiency include:

1) Particle size effect on extraction efficiency, 2) Control of kiln bed temperature (i.e., bed heat transfer) and 3) Solids-gas mixing efficiency (i.e., bed mass transfer). This paper explores these issues for one ex-situ rotary kiln process. For this specific process, the theoretical yields are estimated to be well over 90% while the mechanical reliability remains uncertain. The combination of high process yield plus low mechanical utilization results in an undefined production profile which prevents this process from being fully commercialized.

The work reported in this paper briefly describes an ex-situ process previously developed by Smoot and co-workers [1]. This process is based on an externally heated

horizontal rotary kiln shown to operate with high process efficiency for Oil Shale. The present work focuses on the main concerns related to Critical Operational Issues which prevent further commercialization of this process. In addition, an Aspen diagram of the overall oil shale process is presented as ongoing work required commercializing this process.

1. INTRODUCTION AND BACKGROUND

Conventional petroleum sources are typically those sources which flow freely, when accessed by drilling, due to the pressures in the reservoirs, but Unconventional hydrocarbon sources require additional processing steps to recover the oils including hydro-treating to upgrade the crude into useable liquid transportation fuels. Comparison of world conventional and unconventional oil is shown in Figure 1.1 [3]. Unconventional petroleum reserves include:

Heavy oils, which can be pumped and refined just like conventional petroleum except that they are thicker and have more sulfur and heavy metal contamination, necessitating more extensive refining.

Tar Sands, which can be recovered via surface mining or in-situ collection techniques. Again, this is more expensive than lifting conventional petroleum but not prohibitively so. Canada's Athabasca tar sand is the best known example of this kind of unconventional reserve.

Oil Shale requires extensive processing and consumes large amounts of water. Still, reserves far exceed supplies of conventional oil [2].

Even though heavy oils and oil sands require extra processing which leads to higher costs of recovery, there is still great interest in recovering these resources because of the vast quantities of unconventional oil found in the U.S. and Canada in relation to conventional oil reserves.

Figure 1.2 [4] shows how the addition of unconventional oil deposits, such as U.S. oil shale, Canadian tar sands and Venezuela's extra-heavy oil, greatly affects the world's oil inventory.

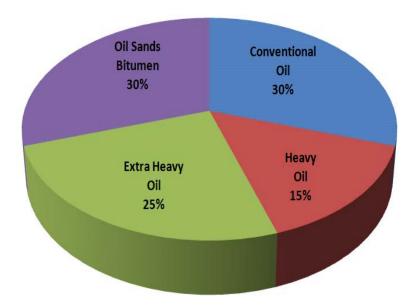


Figure 1.1. Comparison of world conventional and unconventional oil reserves

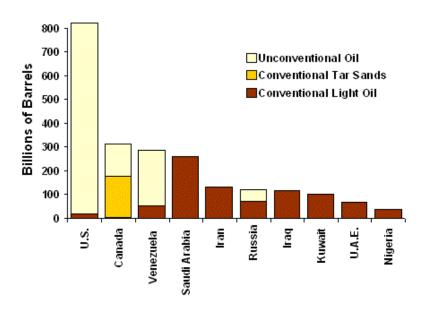


Figure 1.2. Comparison of conventional oil vs. unconventional oil in each country

Several ex-situ processes have been developed and used to produce syn-crude from oil sands/oil shale including: 1) Hot Water Extraction, 2) External Hot Gas, 3) Indirect Heating and 4) Internal Combustion. More recently, several in-situ methods have been explored including: 1) Shell's In-Situ conversion process (ICP), 2) ExxonMobil's Electrofrac process, 3) Petro Probe superheated air method and 4) IEP Geothermal Fuel Cell (GFC).

The major challenge for any new ex-situ or in-situ process is transforming it from a pilot demonstration project to a fully commercial plant. This challenge includes several environmental issues including water usage and treatment, greenhouse gas emissions, and land reclamation. Although tremendous advances have been, many challenges remain including energy efficiency, net water demand, CO₂ generation, reclaiming the land, resource recoverability but most importantly, the many mechanical and operational issues related to on-line reliability.

One issue related to the environmental impact of this ex-situ process is how to use the spent shale (sands). Generally, this material is an excellent source of road base. However, heavy metals leaching from the de-oiled material must be further addressed to reduce production uncertainty. Resolving this uncertainty can help further define the production profile required for commercialization.

Back in 80's and early 90's lots of researches have been done regarding spent oil shale leaching experiment. Most of them used the EPA extraction procedure [5][6] and ASTM D3987 [7] and Two Column test methods as reference method. Also, ground water simulation and organic residual leaching were done in the time.

Another issue required for commercialization is having a comprehensive process model that describes the full process. A fully verified tool is necessary to establish a detailed and clear business plan. This tool, based on process testing, is necessary to establish an acceptable economic risk profile for process commercialization.

2. LECHING METHODOLOGY

The possibility of water pollution from spent oil shale is a problem that should be studied before any significant commercial production is attempted. The hazard to the surface environment is the possibility of the movement of ground water through the Exsitu or In-situ retorted oil shale which may leach harmful minerals, heavy metals and salts from the oil shale [8][9].

In this experiment only one type of spent oil shale was used as a resource for all samples, which had an average size of between 1 to 3 mm and were mostly spherical in shape. The spent oil shale used in this investigation was shipped from Combustion Resources in Provo, Utah where they had been retorted in a horizontal kiln at a flue gas temperature of (650°C). White River shale (medium grade) used as feed to this kiln had a bulk density of 78.6 lb/ft³ with a mean particle size of 1.6 mm which had a gross heating value of 2831 BTU/lb. Heat of pyrolysis was reported as 524 KJ/Kg. 11.09% by weight of the wet shale turned to shale oil with 2.4% water and 1.84% gas. 84.67% by weight were reported as spent oil shale. The produced shale oil from this pyrolysis process had heating value of 15161 BTU/lb [1].

Step 1: An analysis of total organic carbon (TOC) in the spent oil shale sample used is in this leaching investigation was performed and result is presented in Table 2.1. As a standard reference, glucose carbon test was carried out.

Glucose Carbon standard values represent weights of carbon detected in the glucose test sample (contains approximately 40% carbon).

Table 2.1. Total Organic Carbon of Spent	Oil Shale
--	-----------

	Spent oil shale sample (mg)	Peak area	TOC (μg/mg of sample)	Average TOC (μg/mg sample)
SAMPLE1	101.5	787.6	61.4	
SAMPLE 2	78.32	671.2	67.8	64.24
SAMPLE 3	83.43	668.6	63.4	
Spike test	81.75(1)	1290	10.32(2)	Conducted after testing to confirm average results

Table 2.2. Peak area vs. Carbon plot

Glucose Standard Carbon (mg)	0	1.25	2.5	5	10	15	20
Peak Area	0	158.3	300.5	615	1213	1889	2585

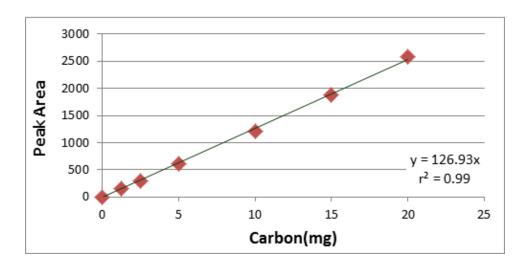


Figure 2.1. Glucose Standard Carbon Test

⁽¹⁾ Mg of sample + 5 mg carbon (2) Expected Value is 10.21 (Test result recovery is 101.03%)

Step 2: Test samples were selected randomly from the resource. Water was used as the leachate and Nitric Acid 3% as a miscible liquid that was mixed with water to approximately simulate ground water[10][11]. Two different pHs were considered for ground water (pH = 4 and pH = 5) plus two different solid to liquid ratio values were considered (S/L = 1/10 and S/L = 1/20).

For the first case, a ratio of 1/10 for solid to liquid was used. To achieve this S/L ratio, 10 grams of spent oil shale (solid) was mixed with 100 grams of water (liquid) with a pH of 4. To get an estimate of experimental error, 5 replications were completed for each test condition. For the second case, the pH was held constant at the same level as used in the first test but the solid to liquid ratio was changed to 1 to 20. This was achieved by mixing 5 grams of spent oil shale with 100 grams water in the sample container. The leachate pH was then increased to 5 for the third test condition with a ratio of 1 to 10 for solid to liquid. Finally the fourth condition was completed using a pH of 5 and a ratio of 1/20 for solid to liquid.

Step 3: The full test considered of 20 sample containers which were left for 24 hours in a shaker operating at 180 shakes per minute.

Step 4: After the 24 hour period, the mixtures were filtered through a special filter (nonsterile syringe filter, pore size 0.2µ) and were placed in ICP-MS.

Inductively Coupled Plasma Mass Spectrometry or ICP-MS shown in Figure 2.2, is designed to detect different various types of elements especially heavy metals with a quantitative measure of their concentration. ICP-MS has many advantages including: 1) Detection limits for most elements equal to or better than those obtained by Graphite

Furnace Atomic Absorption Spectroscopy (GFAAS), 2) Higher throughput than GFAAS and 3) The ability to obtain isotopic information.



Figure 2.2. ICP-MS

3. RESULTS

Two blanks were prepared for the two different pHs used in the test. Table 3.1 shows metal concentration in blanks which were mixture of nitric acid and water. Also the results in four cases which were studied in the "Leaching" experiment are shown below.

Table 3.1. Metals concentration in blanks

		Concentrations in ppb										
Sample ID	Be	Cr	Ni	Cu	Zn	As	Se	Cd	Sb	Ва	Pb	Ti
Blank pH 5	<dl<sup>(1)</dl<sup>	<dl< td=""><td>1.98</td><td>0.27</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1.98	0.27	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.23</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	0.23	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
Blank pH 4	<dl< td=""><td><dl< td=""><td>1.13</td><td>0.61</td><td>1.95</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.13</td><td>0.61</td><td>1.95</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	1.13	0.61	1.95	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.62</td><td>0.09</td><td><dl< td=""></dl<></td></dl<>	0.62	0.09	<dl< td=""></dl<>
Detection Limit	0.02	1.50	1.00	0.20	1.00	0.20	1.00	0.02	0.20	0.05	0.05	0.05

⁽¹⁾ DL stands for Detection Limit

Table 3.2. Case 1, pH=4 and Solid to Liquid ratio=1/10

Sample ID	Concentration (ppb)											
	Be	Cr	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Pb	Ti
Spike 20ppb	14.87	17.34	17.38	16.32	17.77	55.04	31.68	22.01	33.80		18.32	25.24
Spike recovery%	74.35	81.66	77.12	77.33	86.26	105.01	118.55	103.08	108.01		91.52	126.00
1-10 pH 4 A	<dl< td=""><td><dl< td=""><td>2.14</td><td>0.95</td><td><dl< td=""><td>32.02</td><td>9.92</td><td>1.55</td><td>13.08</td><td>118.13</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>2.14</td><td>0.95</td><td><dl< td=""><td>32.02</td><td>9.92</td><td>1.55</td><td>13.08</td><td>118.13</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	2.14	0.95	<dl< td=""><td>32.02</td><td>9.92</td><td>1.55</td><td>13.08</td><td>118.13</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	32.02	9.92	1.55	13.08	118.13	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-10 pH 4 B	<dl< td=""><td><dl< td=""><td>1.96</td><td>0.85</td><td><dl< td=""><td>34.04</td><td>7.97</td><td>1.40</td><td>12.20</td><td>114.70</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.96</td><td>0.85</td><td><dl< td=""><td>34.04</td><td>7.97</td><td>1.40</td><td>12.20</td><td>114.70</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.96	0.85	<dl< td=""><td>34.04</td><td>7.97</td><td>1.40</td><td>12.20</td><td>114.70</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	34.04	7.97	1.40	12.20	114.70	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-10 pH 4 C	<dl< td=""><td><dl< td=""><td>1.75</td><td>0.77</td><td><dl< td=""><td>29.25</td><td>9.65</td><td>1.67</td><td>12.69</td><td>126.64</td><td>0.08</td><td>0.05</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.75</td><td>0.77</td><td><dl< td=""><td>29.25</td><td>9.65</td><td>1.67</td><td>12.69</td><td>126.64</td><td>0.08</td><td>0.05</td></dl<></td></dl<>	1.75	0.77	<dl< td=""><td>29.25</td><td>9.65</td><td>1.67</td><td>12.69</td><td>126.64</td><td>0.08</td><td>0.05</td></dl<>	29.25	9.65	1.67	12.69	126.64	0.08	0.05
1-10 pH 4 D	<dl< td=""><td><dl< td=""><td>2.05</td><td>0.89</td><td>1.03</td><td>29.82</td><td>10.55</td><td>1.60</td><td>12.95</td><td>120.52</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>2.05</td><td>0.89</td><td>1.03</td><td>29.82</td><td>10.55</td><td>1.60</td><td>12.95</td><td>120.52</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	2.05	0.89	1.03	29.82	10.55	1.60	12.95	120.52	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-10 pH 4 E	<dl< td=""><td><dl< td=""><td>1.76</td><td>0.74</td><td><dl< td=""><td>29.38</td><td>9.72</td><td>1.60</td><td>12.95</td><td>130.57</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.76</td><td>0.74</td><td><dl< td=""><td>29.38</td><td>9.72</td><td>1.60</td><td>12.95</td><td>130.57</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.76	0.74	<dl< td=""><td>29.38</td><td>9.72</td><td>1.60</td><td>12.95</td><td>130.57</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	29.38	9.72	1.60	12.95	130.57	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>

Table 3.3. Case 2, pH=4 and Solid to Liquid ratio=1/20

Sample ID	Concentration (ppb)												
	Be	Cr	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Pb	Ti	
Spike 20ppb	16.64	16.19	16.34	15.42	17.65	56.14	30.15	21.12	27.61		16.45	22.05	
Spike recovery%	83.19	77.48	74.86	73.65	86.49	93.73	114.92	101.63	102.35		82.08	110.12	
1-20 pH 4 A	<dl< td=""><td><dl< td=""><td>1.37</td><td>0.69</td><td><dl< td=""><td>37.39</td><td>7.16</td><td>0.79</td><td>7.14</td><td>96.62</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.37</td><td>0.69</td><td><dl< td=""><td>37.39</td><td>7.16</td><td>0.79</td><td>7.14</td><td>96.62</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.37	0.69	<dl< td=""><td>37.39</td><td>7.16</td><td>0.79</td><td>7.14</td><td>96.62</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	37.39	7.16	0.79	7.14	96.62	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
1-20 pH 4 B	0.03	<dl< td=""><td>1.11</td><td>0.66</td><td><dl< td=""><td>37.20</td><td>6.68</td><td>0.86</td><td>7.57</td><td>101.07</td><td>0.10</td><td>0.05</td></dl<></td></dl<>	1.11	0.66	<dl< td=""><td>37.20</td><td>6.68</td><td>0.86</td><td>7.57</td><td>101.07</td><td>0.10</td><td>0.05</td></dl<>	37.20	6.68	0.86	7.57	101.07	0.10	0.05	
1-20 pH 4 C	<dl< td=""><td><dl< td=""><td>1.03</td><td>0.71</td><td><dl< td=""><td>34.95</td><td>7.00</td><td>0.87</td><td>7.70</td><td>103.56</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.03</td><td>0.71</td><td><dl< td=""><td>34.95</td><td>7.00</td><td>0.87</td><td>7.70</td><td>103.56</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.03	0.71	<dl< td=""><td>34.95</td><td>7.00</td><td>0.87</td><td>7.70</td><td>103.56</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	34.95	7.00	0.87	7.70	103.56	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
1-20 pH 4 D	<dl< td=""><td><dl< td=""><td>1.11</td><td>0.68</td><td><dl< td=""><td>30.25</td><td>6.79</td><td>0.83</td><td>7.84</td><td>106.19</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.11</td><td>0.68</td><td><dl< td=""><td>30.25</td><td>6.79</td><td>0.83</td><td>7.84</td><td>106.19</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.11	0.68	<dl< td=""><td>30.25</td><td>6.79</td><td>0.83</td><td>7.84</td><td>106.19</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	30.25	6.79	0.83	7.84	106.19	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
1-20 pH 4 E	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.61</td><td><dl< td=""><td>28.10</td><td>6.44</td><td>0.74</td><td>7.79</td><td>111.02</td><td>0.06</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.61</td><td><dl< td=""><td>28.10</td><td>6.44</td><td>0.74</td><td>7.79</td><td>111.02</td><td>0.06</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.61</td><td><dl< td=""><td>28.10</td><td>6.44</td><td>0.74</td><td>7.79</td><td>111.02</td><td>0.06</td><td><dl< td=""></dl<></td></dl<></td></dl<>	0.61	<dl< td=""><td>28.10</td><td>6.44</td><td>0.74</td><td>7.79</td><td>111.02</td><td>0.06</td><td><dl< td=""></dl<></td></dl<>	28.10	6.44	0.74	7.79	111.02	0.06	<dl< td=""></dl<>	

Table 3.4. Case 3, pH=5 and Solid to Liquid ratio=1/10

Sample ID	Concentration (ppb)											
	Be	Cr	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Pb	Ti
Spike 20ppb	13.72	16.52	16.77	15.60	16.72	48.07	33.60	21.85	34.33		17.58	24.22
Spike recovery%	68.56	79.22	74.82	73.98	81.82	103.63	117.20	100.58	104.19		87.74	120.90
1-10 pH 5 A	0.04	<dl< td=""><td>1.91</td><td>0.84</td><td><dl< td=""><td>28.02</td><td>11.59</td><td>1.75</td><td>16.22</td><td>113.09</td><td>0.08</td><td>0.09</td></dl<></td></dl<>	1.91	0.84	<dl< td=""><td>28.02</td><td>11.59</td><td>1.75</td><td>16.22</td><td>113.09</td><td>0.08</td><td>0.09</td></dl<>	28.02	11.59	1.75	16.22	113.09	0.08	0.09
1-10 pH 5 B	<dl< td=""><td><dl< td=""><td>1.81</td><td>0.80</td><td><dl< td=""><td>27.35</td><td>10.16</td><td>1.73</td><td>13.49</td><td>113.61</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.81</td><td>0.80</td><td><dl< td=""><td>27.35</td><td>10.16</td><td>1.73</td><td>13.49</td><td>113.61</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.81	0.80	<dl< td=""><td>27.35</td><td>10.16</td><td>1.73</td><td>13.49</td><td>113.61</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	27.35	10.16	1.73	13.49	113.61	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-10 pH 5 C	<dl< td=""><td><dl< td=""><td>1.68</td><td>0.88</td><td><dl< td=""><td>32.93</td><td>10.76</td><td>1.48</td><td>14.48</td><td>131.60</td><td>0.07</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.68</td><td>0.88</td><td><dl< td=""><td>32.93</td><td>10.76</td><td>1.48</td><td>14.48</td><td>131.60</td><td>0.07</td><td><dl< td=""></dl<></td></dl<></td></dl<>	1.68	0.88	<dl< td=""><td>32.93</td><td>10.76</td><td>1.48</td><td>14.48</td><td>131.60</td><td>0.07</td><td><dl< td=""></dl<></td></dl<>	32.93	10.76	1.48	14.48	131.60	0.07	<dl< td=""></dl<>
1-10 pH 5 D	<dl< td=""><td><dl< td=""><td>2.03</td><td>0.92</td><td><dl< td=""><td>29.29</td><td>10.70</td><td>1.55</td><td>13.42</td><td>116.35</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>2.03</td><td>0.92</td><td><dl< td=""><td>29.29</td><td>10.70</td><td>1.55</td><td>13.42</td><td>116.35</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	2.03	0.92	<dl< td=""><td>29.29</td><td>10.70</td><td>1.55</td><td>13.42</td><td>116.35</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	29.29	10.70	1.55	13.42	116.35	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-10 pH 5 E	<dl< td=""><td><dl< td=""><td>1.39</td><td>0.84</td><td><dl< td=""><td>31.27</td><td>9.15</td><td>1.38</td><td>12.93</td><td>151.28</td><td><dl< td=""><td>0.06</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.39</td><td>0.84</td><td><dl< td=""><td>31.27</td><td>9.15</td><td>1.38</td><td>12.93</td><td>151.28</td><td><dl< td=""><td>0.06</td></dl<></td></dl<></td></dl<>	1.39	0.84	<dl< td=""><td>31.27</td><td>9.15</td><td>1.38</td><td>12.93</td><td>151.28</td><td><dl< td=""><td>0.06</td></dl<></td></dl<>	31.27	9.15	1.38	12.93	151.28	<dl< td=""><td>0.06</td></dl<>	0.06

Except Be, Cr and Ti other metals were detected very well. By a comparison between case 1 and case 2 it was found that increasing the solid to liquid ration will yield to greater concentration of metals. This is proved for both pHs. To evaluate pH effect on leachability, case 1 and case 3 were considered. As the results show, increasing leachate's

pH affected on some metal's concentration and just a slightly change happened to others.

This also happened to case 2 and case 4.

So it is concluded that for some kind of metals increasing pH of the leachate will yield to smaller concentration of metals, but for many others it is ineffective. Results are shown in Figure 3.1.

Table 3.5. Case 4, pH=5 and Solid to Liquid ratio=1/20

Sample ID	Concentration (ppb)											
	Be	Cr	Ni	Cu	Zn	As	Se	Cd	Sb	Ba	Pb	Ti
Spike 20ppb	15.63		16.30	15.47	17.16	58.24	32.50	21.56	29.99		15.87	21.91
Spike recovery%	78.17		76.26	74.01	84.32	110.19	125.07	103.55	106.40		79.06	109.39
1-20 pH 5 A	<dl< td=""><td></td><td>1.04</td><td>0.66</td><td><dl< td=""><td>36.21</td><td>7.48</td><td>0.85</td><td>8.71</td><td>115.82</td><td>0.05</td><td><dl< td=""></dl<></td></dl<></td></dl<>		1.04	0.66	<dl< td=""><td>36.21</td><td>7.48</td><td>0.85</td><td>8.71</td><td>115.82</td><td>0.05</td><td><dl< td=""></dl<></td></dl<>	36.21	7.48	0.85	8.71	115.82	0.05	<dl< td=""></dl<>
1-20 pH 5 B	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.51</td><td><dl< td=""><td>31.25</td><td>6.56</td><td>0.89</td><td>7.86</td><td>109.53</td><td>0.08</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.51</td><td><dl< td=""><td>31.25</td><td>6.56</td><td>0.89</td><td>7.86</td><td>109.53</td><td>0.08</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.51</td><td><dl< td=""><td>31.25</td><td>6.56</td><td>0.89</td><td>7.86</td><td>109.53</td><td>0.08</td><td><dl< td=""></dl<></td></dl<></td></dl<>	0.51	<dl< td=""><td>31.25</td><td>6.56</td><td>0.89</td><td>7.86</td><td>109.53</td><td>0.08</td><td><dl< td=""></dl<></td></dl<>	31.25	6.56	0.89	7.86	109.53	0.08	<dl< td=""></dl<>
1-20 pH 5 C	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.52</td><td><dl< td=""><td>29.91</td><td>5.69</td><td>0.77</td><td>7.15</td><td>111.42</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.52</td><td><dl< td=""><td>29.91</td><td>5.69</td><td>0.77</td><td>7.15</td><td>111.42</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.52</td><td><dl< td=""><td>29.91</td><td>5.69</td><td>0.77</td><td>7.15</td><td>111.42</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	0.52	<dl< td=""><td>29.91</td><td>5.69</td><td>0.77</td><td>7.15</td><td>111.42</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	29.91	5.69	0.77	7.15	111.42	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-20 pH 5 D	<dl< td=""><td><dl< td=""><td>1.12</td><td>0.61</td><td><dl< td=""><td>38.01</td><td>5.68</td><td>0.83</td><td>7.54</td><td>111.22</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>1.12</td><td>0.61</td><td><dl< td=""><td>38.01</td><td>5.68</td><td>0.83</td><td>7.54</td><td>111.22</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	1.12	0.61	<dl< td=""><td>38.01</td><td>5.68</td><td>0.83</td><td>7.54</td><td>111.22</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	38.01	5.68	0.83	7.54	111.22	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
1-20 pH 5 E	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.53</td><td><dl< td=""><td>35.64</td><td>6.92</td><td>0.82</td><td>7.79</td><td>113.47</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.53</td><td><dl< td=""><td>35.64</td><td>6.92</td><td>0.82</td><td>7.79</td><td>113.47</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.53</td><td><dl< td=""><td>35.64</td><td>6.92</td><td>0.82</td><td>7.79</td><td>113.47</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	0.53	<dl< td=""><td>35.64</td><td>6.92</td><td>0.82</td><td>7.79</td><td>113.47</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	35.64	6.92	0.82	7.79	113.47	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>

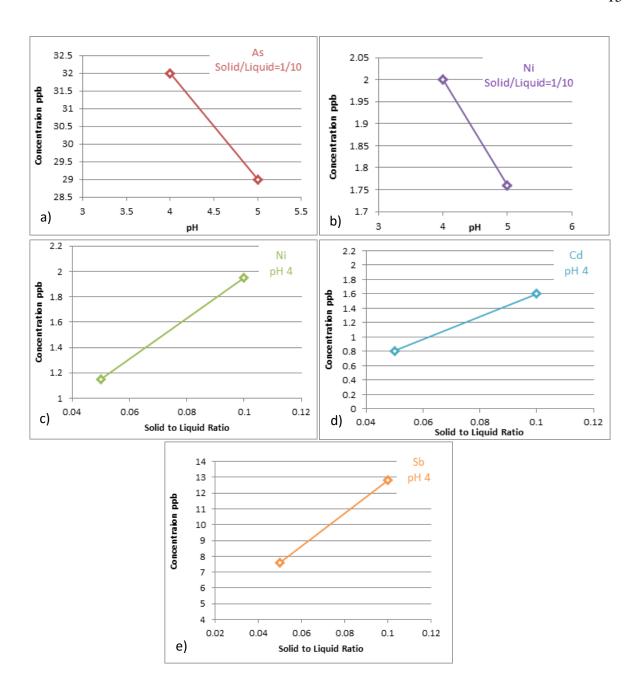


Figure 3.1. Metal concentration for various conditions

4. FUTURE WORK

To bring any new process to commercialization, several key questions and issues have to be addressed [12][13]:

- 1) Develop general process description and block flow diagram,
- 2) Gather process chemistry and thermodynamics for each major process unit,
- 3) Perform pilot plant experiments to gather process data,
- 4) Develop a detailed process description including detailed flow diagrams with mass and energy balances for the major process variations and feeds and
- 5) Provide a summary of the process with the process cost per unit of product; energy efficiency; cost of water, electricity, and other utilities per unit of product.

Following aspen diagram shows an overall process of oil shale in a vertical retort in Figure 4.1. Some modifications have been done on previous models which are discussed below.

As it is shown, raw oil shale and hot nitrogen (inert) are described as feed to Dryer. In this block the shale is heated up to 200-250°C and the moisture gets out through exhaust stream. Then dry shale as a product of dryer will be sent to pyrolysis block as a feed. The temperature in pyrolysis part goes up to 500-600°C and hydrocarbon vapors (HV) will be extracted from shale. Sufficient heat for this block is supplied from combustion block (800°C) in addition to a limited amount (prevent burning and combustion) of hot air comes directly through a compressor and heater. Hydrocarbon vapor and spent oil shale are considered as product of pyrolysis block. HV will be transported to sweeting unit for desulfurization and then nitrogen is separated from HV. After nitrogen and sulfur separation, remaining hydrocarbon vapor will be sent to a separator which separates the

condensate (Kerogen) from non-condensable gas. A fraction of this gas will be sent to combustor as a part of fuel feed.

Kerogen is a pyrobitumen, and oil is formed from kerogen by heating. It consists chiefly of low forms of plant life; chemically it is a complex mixture of large organic molecules, containing hydrogen, carbon, oxygen, nitrogen, and sulfur. Kerogen is the chief source of oil in oil shale. Finally after shale oil is produced, it is sent to upgrading unit. Shale oil upgrading generally includes additional processing equivalent to crude oil hydrocracking (required to convert oil shale distillates to gasoline). Upgrading also removes arsenic and nitrogen applying hydro-treating.

A small part of the spent oil shale as a product of pyrolysis section is separated and sent to combustor as a part of feed. To control CO₂ emission, it is recommended to use a small amount of spent oil shale as fuel in combustion unit. The remaining spent oil shale can be used for many purposes containing road basement. So one of the most important issues related to spent shale is the leachability which were studied and discussed.

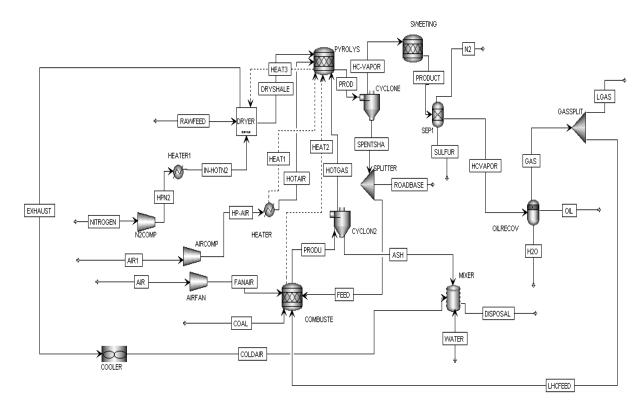


Figure 4.1. Overall Oil Shale Vertical Retort, Aspen Model Diagram

5. CONCLUSION

The leachability of heavy metals in spent oil shale was studied and it was introduced as an environmental issue. The results of leaching test illustrate the impacts of solid to liquid ratio and pH increasing on the leachability of heavy metals and their concentration in the leachate. Key mechanical issues that affect online reliability and process efficiency include: particle size effect on extraction efficiency, kiln bed temperature control (i.e., bed heat transfer), solids/gas mixing efficiency.

Many necessary steps are needed to bring a new process to commercial operation such as developing a detailed process description including detailed flow diagrams with mass and energy balances for the major process variations and feeds. However, this work is only preliminary and a far more detailed and accurate analysis will be possible once better design data can be obtained.

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II. OPTIMIZING REACTOR PARAMETERS TO ACHIEVE HIGHER PROCESS YIELD IN EX-SITU OIL SHALE PROCESS

ABSTRACT

Declining worldwide crude oil reserves and increasing energy needs has focused attention on developing existing unconventional fossil fuels including oil shale. America's richest oil shale deposits are found in the Green River Formation of western Colorado, eastern Utah and south-western Wyoming. The current work describes process simulation of an ex-situ oil shale pyrolysis process in a pyrolytic reactor using a novel method involving external and internal heating to increase heat transfer and mixing ratio inside the reactor.

Efforts to improve process yield for commercial operation relies on first developing a complete Aspen based process model of a proposed shale refining plant, identifying the key process parameters for the reactor and then optimizing the overall process. Simulation results are compared to earlier experimental data collected from a pilot scale rotary reactor operated by Combustion Resources, Inc. This work identified the critical impact of bed temperature on crude production in such a way that for a bed temperature of less than 400°C, results showed less than 10% conversion in crude production and for bed temperatures between 450-500°C, above 90% conversion was achieved while minimizing carbon dioxide formation from carbonate minerals inside the shale. The residence time for oil shale pyrolysis process in the reactor was also shown to be a critical parameter which can be controlled by manipulating other key parameters like raw oil shale feed rate and also the bed temperature. The focus of this work was to optimize the rate of production of

syncrude from oil shale which also enhanced process environmental and economic sustainability.

Aspen simulation of oil shale process is an effective process modelling tool to optimize the overall process. The model has kerogen, minerals and moisture combined together to define oil shale composition. The proposed model consists of three zones including drying, combustion and reactor zone which are simulated separately. Different cases are defined and studied based on various operational conditions. As a result, optimized operational values for the key parameters and also some recommendations to this process are given.

1. INTRODUCTION AND BACKGROUND

Oil shale is a sedimentary rock which under a high temperature process in a very low controlled amount of oxygen called "pyrolysis" starts to devolatilize a combustible fuel gas called "synthesis gas" which further could be converted to liquid fuel or a variety of useful chemicals in a chemical refinery. Kerogen has a high hydrogen-to-carbon ratio, giving it the potential to be superior to heavy oil or coal as a source of liquid fuel [1]. Shale breaks into thin pieces with sharp edges. It occurs in a wide range of colours that include: red, brown, green, grey, and black [10]. In ex-situ process, oil shale rocks are mined and crushed to fine particles before processing as shown in Figure 1.2 [12]. Oil shale is spread across the world. United States of America has the highest deposit of oil shale as shown in Figure 1.3 [9]. This hydrocarbon resource represents a major energy reserve and can increase U.S. energy security and support sustained economic growth. Various extraction processes have been developed but none yet has been commercialized to produce synthetic crude from oil shale deposit. Australia's attempt to commercialise oil shale plant has been through the Stuart Oil Shale Project developed by Southern Pacific Petroleum NL [13]. Oil shale retort of Stuart Oil Shale plant is shown in Figure 1.4 [11]. Pharaoh indirect heating retort is shown in Figure 1.5 [14].



Figure 1.1. Left to right: Utah oil shale, Estonian oil shale, Jordan oil shale



Figure 1.2. Crushed Oil Shale

The study about how changing reactor parameters affect the overall performance of oil shale processing from Utah oil shale is based on indirectly gas-heated reactor where oil shale inside the reactor is heated through a barrier wall. Combustion chamber consists of air inlets and gas nozzles. Energy released from natural gas combustion process is transferred to reactor by convection and conduction heat transfer. In the drying zone of reactor, crushed raw shale particles (< 2 mm) are mixed with recycle stream of spent shale which act as a heat carrier. Spent shale as a by-product, is heated to (300-600°C). The spent shale could be used as granular fill or sub-base in cement industry [6]. In an indirectly heated reactor the heat tube is inside the case and feed is processed inside the reactor. Pilot plants are usually designed for continuous operations.

Experimental results at the CR pilot plant concluded that the residence time decreases with increased mass flow, but not substantially [5]. Also, it was observed that having a constant heat duty from combustion resource, increasing the feed rate led to lower spent shale temperature and lower shale oil conversion percentage [5].

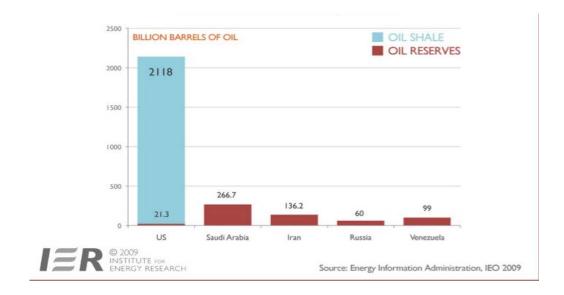


Figure 1.3. Comparison of US Oil Shale Resources with Foreign Oil Reserves



Figure 1.4. Stuart Shale Oil Plant

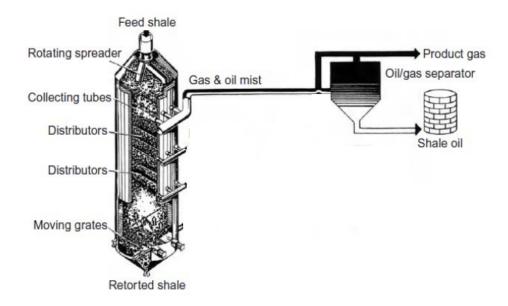


Figure 1.5. Pharaoh retort - Indirect Heating Mode

The United States Government and Environmental Protection Agency (EPA) are planning to regulate high carbon dioxide tax to control green gas house emission in power plants. When the reactor is operating below a certain temperature, the release of CO₂ from carbonates for green river basin oil shale is very low [7]. Increase in the reactor temperature slightly above this specific temperature would produce significantly more CO₂, thus it is important to study how bed temperature affects the release of CO₂. CR process is known to release as low as (< 10%) carbon dioxide.

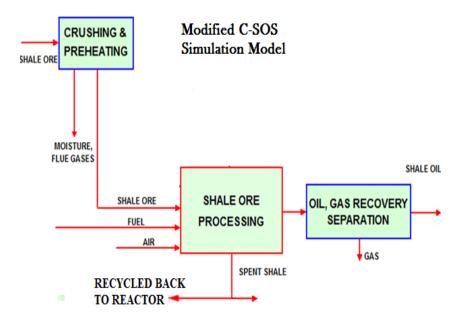


Figure 1.6. Modified C-SOS Model for Simulation

2. ASPEN SIMULATION

Aspen Simulation is used to describe the model for oil shale process and optimize the reactor parameters. Drying zone, reactor zone and the combustion zone are simulated separately and finally integrated as one model.

2.1 DRYING ZONE

Green river oil shale typically consists of 1-2% moisture by weight. Due to low moisture content, the heat duty required for drying zone is not comparable to reaction zone. A heater and a water vapour separator describe the drying section with the heat duty provided from the natural gas burner. The duty from the natural gas burner is split between the drying zone and reaction zone using F-Split. The splitter ratio is set in such way that there is no moisture content in the oil shale feed stream to pyrolysis reactor. The parameters which control the flash separation in the heater are pressure and heat duty. Pressure drop is set to zero and heat duty is controlled by natural gas consumption rate. Before entering the pyrolysis reactor, oil shale feed stream typically has a temperature range from 370 to 400K.

2.2 REACTION ZONE

Reaction zone is the essence and core of oil shale process. Oil shale typically has 20% Hydrocarbon, 1-2% moisture and the rest consists of carbonaceous minerals. There are two kinds of reaction taking place in reaction zone. One is the pyrolysis where the kerogen is converted into light gas and heavy oil. The other one is the decomposition of minerals which is a major contributor to carbon dioxide emission.

In Aspen Simulation there are different types of streams defined, which have to be carefully selected. We chose to have a Mixed, Non-conventional and CI solid stream

(MIXNICI). Oil shale stream is defined as a combination of all these three streams. Moisture is defined as a Mixed Stream whereas kerogen and char as a non-conventional stream and minerals were introduced in a CI solid stream. Table 2.1 shows elemental analysis of kerogen and char [4].

Table 2.1. Elemental Analysis of Kerogen and Char

Element	Kerogen	Char
Carbon	80.972	87.066
Hydrogen	10.193	3.069
Nitrogen	2.361	5.686
Oxygen	5.393	2.320
Sulfur	1.081	1.86

Pyrolysis Reaction: Using a kinetic CSTR reactor, the pyrolysis reaction is modelled on the basis of Diaz and Braun model for a staged, fluidized bed oil-shale retort with lift-pipe combustor. According to the model [2]

$$R(k) = k. Fko. \left(\frac{Fk}{Fko}\right)^n \tag{1}$$

Where:

 $R(k) = \text{kerogen reaction rate, } kg/m^3.s$

 $K = rate constant, s^{-1}$

Reaction constant is given as $k = 6.9*10^{10}e^{((-21790)/T)}$, where T is in Kelvin (2)

 Fk_0 = initial kerogen concentration, kg/m³shale.

 $Fk = final kerogen concentration, kg/m^3shale.$

n = reaction order = 1.4

The production of gas, oil, and char from kerogen pyrolysis is calculated by means of stoichiometric factors, as shown: [2]

R= reaction rate (kg product/m³. s)

$$R=f.R(k) \tag{3}$$

f = stoichiometric factor of (kg product/ kg .s)

Table 2.2 shows the modified stoichiometry for the reaction products [8].

Since Hydrocarbon reaction model is not pre-defined in Aspen plus, the model is written in FORTRAN subroutine [8].

Mineral Decomposition: The Minerals considered in this model are based on the green river oil shale composition given by Brons.et al.1989 [3]. The mineral reactions for the above inorganics defined in Table 2.3 are given as follows:

Analcite: NaAlSi₂O₆. H2O → NaAlSi₂O₆ + H₂O

Siderite: $3FeCO_3 \rightarrow FE_3O_4 + CO + 2CO_2$

<u>Illite</u>: $K(Al_2)(Si_3Al)O_{10}(OH)_2 \rightarrow KAlSi_3O_8 + Al2O_3 + H_2O_3$

High Temperature Reactions

<u>Dolomite</u>: CaMg(CO₃)₂→CaCO₃ + MgO + CO₂

Calcite: $CaCO_3 \rightarrow CaO + CO_2$

Mineral reactions are thermal decomposition reactions and our interest lies in finding the temperature range at which carbon dioxide emission does not occur in a high

rate. To do this we consider the mineral reactions to be thermodynamically modelled using Gibbs reactor.

Table 2.2. Modified Stoichiometry for the Reaction Products

Components	Stoichiometry
H ₂	0.001
H ₂ 0	0.0268
H ₂ S	0.001
NH ₃	0.001
СО	0.0057
CO ₂	0.0359
CH4	0.0142
C ₂ H ₆	0.0118
C ₃ H ₈	0.0117
C4H ₁₀	0.0117
OIL	0.4767
CHAR	0.4025

Reaction equilibrium is calculated based on minimizing Gibbs free energy. Both mineral and pyrolytic reactors are maintained at same temperature in each case. Using a component splitter, the products exiting the pyrolytic reactor can be separated into two

streams as hydrocarbon gas and non-hydrocarbon gas which includes H₂S, NH₃, CO and CO₂. The HC gases are transported to a recovery section whereas the rest of gases are sent into the mineral decomposition reactor. In real process there are only two outlets coming out of the reactor 1) Gas, 2) Spent shale (solid residue). In this simulation we considered three outlets which include: - Hydrocarbon products, Carbon di-oxide and Spent shale solids.

Table 2.3. Composition of Oil Shale

Component	MW g/gmol	wt % Dry basis
Siderite	115.9	2.4
Dolomite	184.4	22.8
Calcite	100.1	14.1
Illite	398.3	10.9
Analcite	220.2	0.9
Dawsonite	144	0.6
Pyrite	120	1.6
Quartz	60.1	13.2
Albite	262.2	13.7
Kerogen		19.8
Total		100

2.3 SPENT SHALE RECYCLE STREAM

The energy required for pyrolysis reaction is provided by the natural gas burner. Our aim is to reduce external heat duty provided by the natural gas burners which in turn reduces the natural gas consumption and further reduces carbon dioxide emission. One approach is to recycle the spent shale back to the reactor as a heat carrier to increase heat transfer and also the mixing ratio in raw feed stream. The amount of spent shale recycled is an important factor which is very much dependent on of the feed flow rate and volume of the reaction zone.

2.4 OIL GAS RECOVERY SECTION

To extract shale oil from produced hydrocarbon gas, an oil recovery section was modelled. In this section, a flash separator is used with a temperature of 300K to do the condensation process. After condensation process, almost 80% of hydrocarbon gas goes to liquid and rest are light gases. The flash separator has 3 outlets: 1) Light Gas, 2) Shale Oil and 3) Water. The overall Aspen simulated model is shown in Figure 2.1.

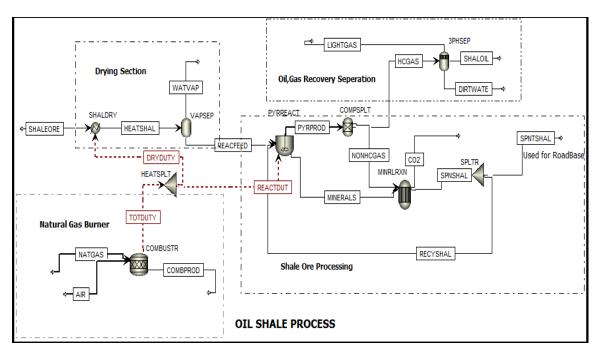


Figure 2.1. Aspen Simulated Model

3. SIMULATION RUN AND RESULTS

Case 1: Fixed Volume, Fixed Feed Rate, Variable Temperature

(Volume of pyrolytic reactor: 0.05 m³ - Feeding rate of oil shale: 26tpd)

The objective of this run is to find the optimum reactor bed temperature for the oil shale process. We define the optimum point here as point of maximum shale oil production and minimum carbon dioxide production. The conversion of kerogen changes from 600K to 873K. The temperature is varied between 600-1273K. Even though we have simulated both reactors separately, the temperatures of both reactors are the same. Also heat duty required for the reactors are in direct relation with natural gas consumption.

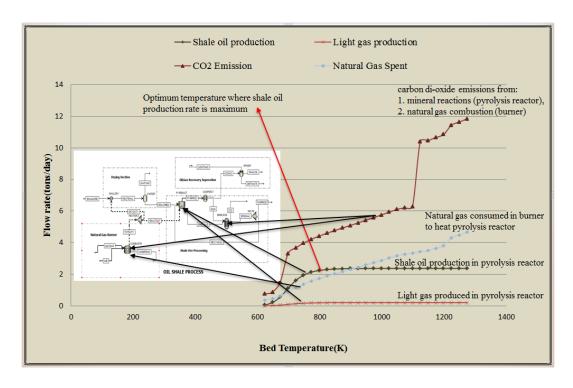


Figure 3.1. Rate of production of shale oil, light gas, CO₂ and natural gas burnt

Sensitivity analysis has been done in Aspen to record the shale oil production, light gas production, natural gas consumption and carbon dioxide production from both reactors corresponding to temperature change. The values are formatted in excel and graphs are plotted here as results.

The pyrolysis reaction is kinetically modelled and so is a function of temperature. From Figure 3.1, it is noticeable that the kerogen conversion increases from 600K to 900K and becomes steady and constant after 900K. The carbon dioxide production on the other hand has more critical points. The largest contribution of carbon dioxide comes from calcite and dolomite. The dolomite decomposition is said to happen at a peak temperature of 1063 K while the calcite decomposition happens from 1133 to 1283K [3].

In our model, there are two critical points for carbon dioxide emission. The graph for carbon dioxide emission from reaction zone is shown in Figure 3.2. The two critical points are at 673.15 K and 1098.15K. The first point is where the dolomite decomposition starts and 1098K is where the calcite decomposition takes place. The dolomite decomposes to calcite which further decomposes to CaO and CO₂ at 1098.15K. This is the reason why we see a sudden hike at 1123.15K.

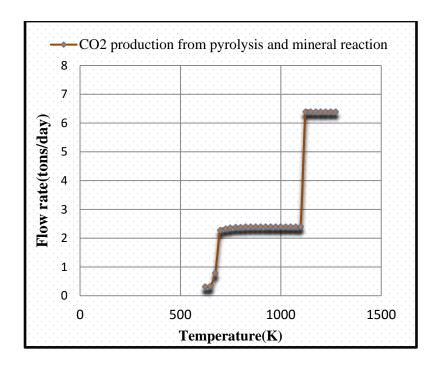


Figure 3.2. CO₂ Production from Pyrolysis and Mineral Reaction

Case 2: Fixed Volume, Limited Heat Duty, Fixed Temperature, Variable Feed Rate

(Volume of reactor: 0.05 m³ - Reactor temperature: 873K - Limited reactor heat duty: 1.46E6 BTU/hr)

The objective of this run is to find the optimum feed rate for a given reactor volume. The volume is fixed as 0.05 m³ and the temperature considered to be the optimum temperature found from results of Case 1: 873K. Feed rate of raw shale is changed from 5 to 50 tpd with a step change of 5 tpd. As feed rate increases, residence time goes down but as far as enough heat is supplied from heating source, the conversion remains the same and shale oil production increases proportionately. This, in reality is possible but limited. What actually happens is when you increase the feed rate, heat duty increases as well but natural gas burners has limited capacity. Based on this fact, the limit for heat duty is assumed to be 1.46E6 BTU/hr.

This experiment indicates that the above chosen heat duty is sufficient for a feed rate of 25 tpd for reactor temperature to be maintained constant at 873 K. As feed rate goes beyond 25 tpd, the shale oil production increases accordingly if there is no constraint on heat duty. To put a constraint, now we fix the heat duty as 1.46E6 BTU/hr and run the simulation for other flow rates.

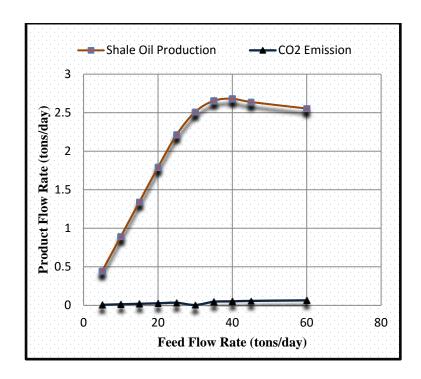


Figure 3.3. Optimising Flow Rate

We notice a temperature drop from 873K. The important fact to be noted at this point is that both reactors have to be maintained at the same temperature. To achieve this, we record the calculated temperature for pyrolytic reactor in each run and apply this temperature on the mineral decomposition reactor. This gives us a good estimate of the

CO₂ production as well. The simulation is run again to find the final shale oil and carbon dioxide emission.

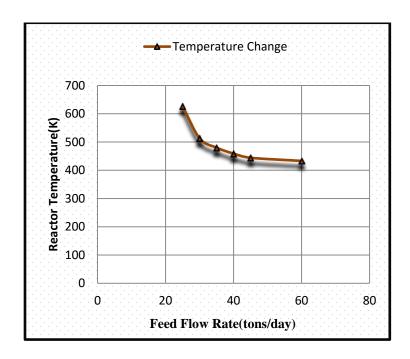


Figure 3.4. Reactor temperature change with feed flow rate at fixed heat duty

When we increase the flow rate with a heat duty fixed at 1.46*E6 BTU/hr, the temperature decreases as shown in Figure 3.4. At this heat duty, the graph in Figure 3.3 indicates that above 25 tpd, the shale oil formation increases till the flow rate reaches 40 tpd above which there is a decline in the shale oil production occurring due to very low temperature.

This experimental run shows that the optimum flow rate for reactor volume of 0.05 m³ and reactor duty of 1.46E6BTU/hr is 40 tpd. If the reactor temperature is maintained at 873K, the corresponding optimum flow rate is 25tpd.

The case 1 gives an optimum temperature for fixed volume and flow rate and case 2 gives optimum flow rate for a fixed volume and temperature along with a heat duty limit.

Next is to find best combination of temperature and flow rate to maximize shale oil production which is discussed in case 3.

Case3: Fixed Volume, Variable Temperature, Variable Feed Rate, Limited Heat Duty (Reactor volume: 0.05 m³ - Limited reactor heat duty: 1.46E6 BTU/hr)

The procedure for case 3 is similar to case 2 but for each single temperature we are going to run the reactor applying different feed to find the best treatment combination of temperature and feed rate which gives us the maximum shale oil production. The graphs are plotted for different temperatures.

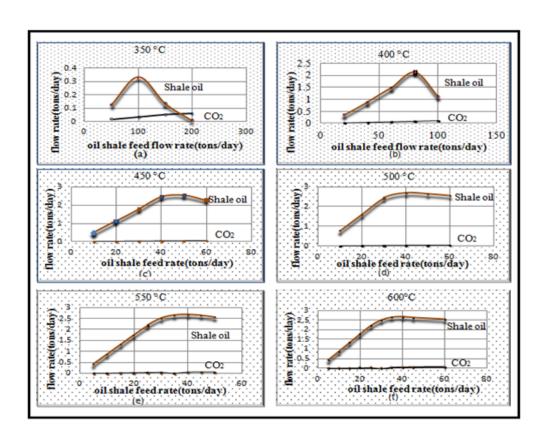


Figure 3.5. Optimizing Temperature and Flow Rate

At 350 °C the shale oil production peaks at 0.3 tons/day as shown in Figure 3.5.a. This production level is very low. At 400°C shale oil produced climbs to 2.2 tons/day shown in Figure 3.5.b. It is shown that 50 degree temperature rise has an enormous increase in shale oil production but other noticeable factor is the reduction in the feed flow rate at peak point.

In Figure 3.5.a, we found that shale oil production peaks at 100 tons/day but in Fig 11-b the peak is seen at 80 tons/day. As the temperature increases, the shale production increases and the feed flow decreases. As emphasized above, the temperature is a crucial factor. When temperature increases, the flow rate decreases to minimize the heat duty. We could have concluded that shale oil production peaks at a point where the temperature is maximum for provided energy. Here we realise the importance of case 1 which showed us that the maximum temperature where shale oil production can reach is 873K, above which we see a level out for a given volume and flow rate. Hence we conclude that, given an energy constraint to the system, there is an optimum point for temperature and flow rate at which shale oil production maximises.

After analysing all the graphs, we see that the maximum shale oil production is 2.68 tpd at 40tpd shale feed rate and a temperature of 458°C. We can conclude that for a 0.05 m³ volume reactor and a maximum heat duty of 1.46*E6 BTU/hr from natural gas burner, the most optimum temperature is 458°C and the corresponding optimum feed rate is 40 tpd.

Case 4: Fixed optimum Temperature, Fixed optimum Feed Rate, Limited Heat Duty (Reactor Volume? - Limited reactor heat duty: 1.46E6 BTU/hr. - Flow rate: 40 tpd)

The objective of case 4 is slightly different from others. Since the reactor volume cannot be changed or be optimized once the plant is built, case 4 is focused on designing the size of the reactor before fabrication. In a situation where we are going to build a new oil shale reactor, the most important constrain that needs to be fixed is maximum energy supply energy. As mentioned before in previous cases, let us consider a natural gas burner which can provide a maximum heat duty of 1.46*E6 BTU/hr to the reactor.

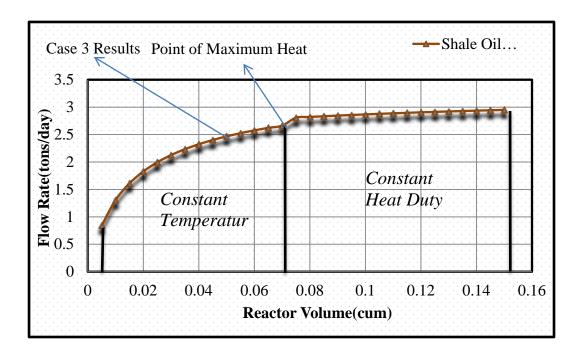


Figure 3.6. Optimizing Reactor Volume

4. CONCLUSION

The oil shale process model developed in Aspen gives an objective to find the optimum temperature and flow rate has been satisfied. The single reactor equipment has been simulated in 3 different zones separately. The model analysis tool of Aspen has been used extensively to find the optimized operating conditions. Three different cases have been studied to find the optimum operating conditions. The first case, gave us a rough estimate of best reactor bed temperature. The focus was more on temperature range of kerogen conversion and carbon dioxide formation without having a limit on heat duty. Case 1 gave a very good estimate of working temperature considering the mineral decomposition reaction. Using the case 1 result of optimum temperature, we found out the best flow rate according to this temperature in case 2. The shale oil production increases with increase in flow rate till the heat duty limit. After this point, we can expect the shale oil production to come down due to decrease in temperature. This gave us the optimum flow rate for a given temperature and reactor volume. Case 3 was performed to find out the best temperature and feed rate for a given reactor volume and limited heat duty. The procedure for case 2 is repeated for different temperatures which constitutes case 3. This is the most critical sensitivity analysis and it concluded that for a 0.05 m³ volume of reactor and 1.46*E6 BTU/hr natural gas burner, the most optimum temperature is 458°C and the corresponding optimum flow rate is 40 tons/day.

Another parameter which could be analysed is the reactor volume. The true significance of this analysis is felt only if it is done before setting-up the plant. Energy requirement and handling capacity for the plant is fixed. For reactor volume of 0.05 m³ and flow rate of 40 tons/day the best yield was 2.68 tons/day of oil, but also at 0.075 m³ the

shale oil yield showed to be 2.8 tons/day, a 5% increase in yield. It is concluded that volume of the reactor definitely plays an important role in process yield. Once the heat duty limit is reached, the percentage increase in shale oil production is not much significant with increase in volume.

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III. PRODUCTION OF SYNGAS FROM BIOMASS USING A MOVING BED DOWNDRAFT REACTOR

ABSTRACT

The role of biomass in energy and fuel production as an alternative to fossil fuel becomes vital especially considering the concern of carbon dioxide production vs. energy use. Sustainable, renewable and reliable resources of domestically produced biomass comparing to wind and solar energy is a sensible motivation to establish a small-scale power plant using biomass as feed to supply electricity demand and heat for rural development. The present work focuses on:

- 1. Design and operation of a vertical downdraft reactor,
- 2. Establishing an optimum operating methodology and parameters to maximize syngas production through process testing.

The down draft reactor design is based on previous work completed at Brigham Young University-Idaho and subsequent design optimization to enhance the operating flexibility for biomass at a one ton per day rate. The reactor is equipped with internal heat transfer surfaces to enhance intra-bed heat and mass transfer inside the reactor. Three different woody biomass feedstocks including pellets, picks and flakes have been examined in this work.

Specific work described in this paper focuses on identifying and characterizing the key operating factors (i.e., temperature profile, feed stock carbon/hydrogen mass ratio, air flow, and residence time) required to optimize yield from this reactor system. To achieve the maximum production yield, experiments were developed and carried out based on classical experimental design methodology.

1. INTRODUCTION AND BACKGROUND

Energy is the major facilitator of the modern life. Every developed and developing economy requires access to advanced sources of energy to support its growth and prosperity. Nowadays, the present energy services have enhanced the living in innumerable ways making an inseparable relation between global population and its dependence on energy production. The relation between world population and its demand on energy growth is shown Figure 1.1 [1].

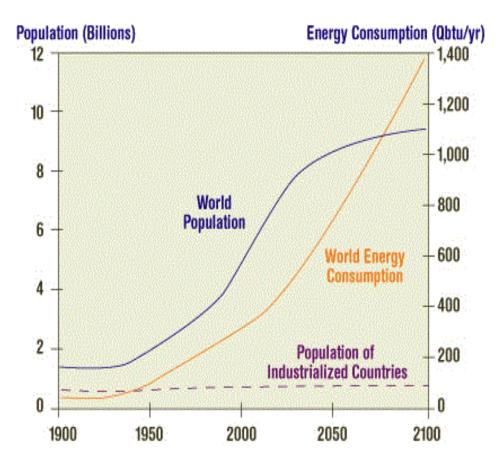


Figure 1.1. World population and energy demand projections

However, the period of flexible supply of energy resources to meet its demand has been falling recently due to its enormous consumption. Fossil fuels being a natural resource are the primary source of energy. The three major fossil fuels coal, oil and natural gas contributes to around 87% of fossil fuels in global energy consumption [2]. Fossil fuels are generally considered as non-renewable source of energy as they cannot be re-generated at a rate adequate for sustainability. The depletion in fossil energy fuels compel mankind to look for alternative energy sources to meet the world demands [4].

The transition from non-renewable energy to renewable energy is increasing, as there is a raise in number of alternative renewable energy choices such as solar, wind, biomass and geothermal energy. Recent studies show that there is a 6% increase in use of renewables in total primary energy supply in two decades spanning from late 90's to 2020 [5]. Apart from their depletion, fossil fuels when burnt release greenhouse and poisonous gases such as carbon dioxide, Sulphur dioxide, carbon monoxide, nitrogen oxides etc. having a severe impact on the environment. In United States, about 90% of the greenhouse gases are due to combustion of fossil fuels [6]. Biomass, being one of the renewable energy sources, can be viewed as a substitute for fossil fuel to cope with the increasing energy demand. In 2010, the renewables accounted to 16.7% in the world energy consumption of which biomass contributes to about 70% of renewable energy as shown in Figure 1.2 [7].

1.1 BIOMASS GASIFICATION

Biomass is biological organic matter derived from the dead or living organisms composed of molecules of carbon, hydrogen, oxygen, nitrogen and small amount of Sulphur and other heavy metals. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel.

The three main sources of biomass are woody biomass, non-woody biomass and animal or mankind. Among all of these, wood remains as the largest source of biomass energy [8]. It is also a viable option for the substitution of coal in industrial combustors and gasifiers as it is a large sustainable energy resource.

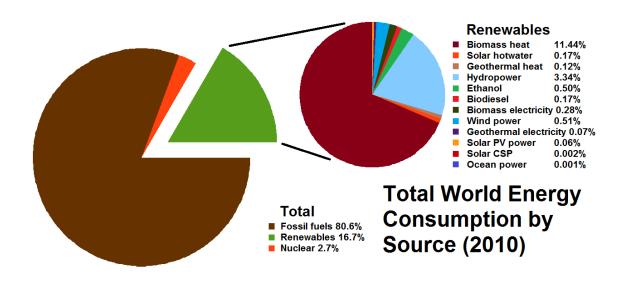


Figure 1.2. World energy consumption by source

To reduce harmful emissions, the variation of fuels is not the only solution. Other options include different conversion processes and variation in the technologies carrying out such conversions is also required. Among the technologies available for using biomass for producing energy, gasification is relatively new which is considered as an environmentally benign solution.

Gasification is primarily a thermo-chemical conversion or incomplete combustion of carbonaceous material at elevated temperatures. In general, the production of heat or power with comparatively high efficiency with low-value or waste feedstocks such as

biomass, refinery residues, municipal wastes and any carbonaceous compounds can be referred as gasification process. This is achieved by reacting the material at high temperatures with a controlled amount of air, oxygen or steam. The biomass gasification process contains a series of steps: drying, pyrolysis, Combustion and reduction which include exothermic and endothermic reactions to produce the final gas product. During this process, a steady state will be reached and the gasifier will maintain its operation at a certain temperature profile [9]. Biomass gasification being CO₂ neutral is one of the hopeful solutions amongst other renewable sources of energy with many environmental advantages. This is because the carbon content of biomass is absorbed by the CO₂ of the atmosphere making the net CO₂ production to be zero [10]. The product of gasification is called syngas and/or product gas which is a mixture of combustible gases such as CO, CH₄ and H₂. All these reasons make biomass gasification a promising alternative for heat and power generation.

1.2 TYPES OF GASIFIERS

Several biomass gasification reactor designs have been developed and can be generally classified into three broad categories; namely, fixed bed and fluidized bed. Various types of gasifier designs are briefly explained below [11].

Fixed Bed Gasifier (Updraft and downdraft): The fixed bed is filled with carbonaceous material and is classified based on the flow of gasifying agent such as air/steam in the gasifier [12].

Updraft Gasifier: These are one of the oldest and simplest designs of gasifier where the biomass comes from the top while air is entering from the bottom, which is also known as counter flow gasification. The biomass fed at the top of the gasifier is undergoing drying followed by pyrolysis, where the volatile free biomass descends to undergo further process below the pyrolysis zone.

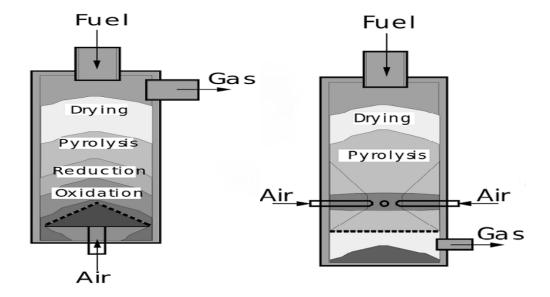


Figure 1.3. Left to right: Fixed bed up draft and down draft biomass gasifier

The grate present at the bottom acts as a support for carbonaceous bed where combustion/oxidation reactions happen above which the reduction/gasification reactions takes place as shown in Figure 1.3 [13]. The hot syngas produced in the gasification zone passes through the pyrolysis and drying zones to provide heat to process raw feedstock present on the top of gasifier. This internal heat exchange between hot syngas and biomass feed leaving behind low temperature exit gas is the main advantage of updraft gasifier. These are also one of the simple and low cost gasifier but the main disadvantage being the syngas produced has to be cleaned of tar, as the syngas produced in the reduction zone leaves the gasifier along with some tars and volatiles while ascending through the pyrolysis and drying zone [14].

Downdraft Gasifier: In downdraft gasifier, air acting as a gasification medium and moves in the same direction as the biomass feed entering from the top, which is also referred as co-current gasification. As shown in Figure 1.3, the grate acts as a support to carbonaceous bed, where the reduction reactions happen followed by combustion, pyrolysis and drying process on the top respectively. The main advantage of downdraft gasifiers is, the tar products that are formed in the pyrolysis zone pass through the glowing charcoal bed where it undergoes reduction reactions to produce tar free gases. The disadvantage being, low density feedstock causes transportability or flow problems and excessive pressure drop which will be discussed in detail in results and discussion [3],[15]. Fluidized Bed Gasifier (bubbling bed, circulating fluidized bed): As shown in Figure 1.4 [17], in fluidized bed gasifier the feedstock particles are fed from the side of gasifier to the preheated granular (sand) bed, where the air/oxygen or steam is blown from the bottom to suspend the biomass particles throughout the gasifier [12],[16].

The upward drag force of gas acting as a fluid causes the suspended solid particles inside the gasifier to mix thoroughly, thereby increasing the solid fluid interaction when compared to fixed bed gasifiers. The major advantage of fluidized bed gasifiers over fixed bed is due to the uniform temperature distribution in the gasification zone which is achieved due to circulating fluid in fine granular material. The loss of fluidization due to accumulation of bed is the major disadvantages of the fluidized bed gasifier [3].

Entrained Bed Gasifier: A dry pulverized solid, an atomized liquid fuel or fuel slurry is gasified with oxygen in co-current flow configuration. The gasification reactions take place in a dense cloud of very fine particles.

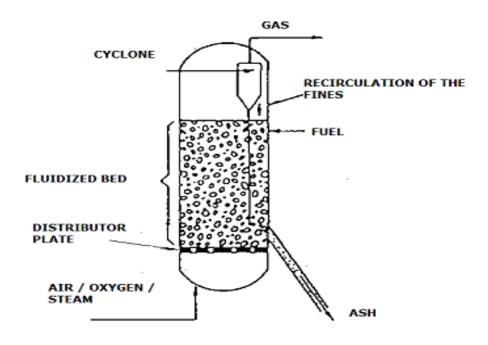


Figure 1.4. Fluidized bed gasifier

During the gasification such unit achieves high temperatures for which tar and methane are not present in the producer gas. The major part of the ash is removed as a slag because of the high operating temperature which is above the ash fusion temperature. However, an entrained-flow gasifier does have disadvantages that requires the highest amount of oxygen and produces the lowest heating value product gas. Entrained flow gasifiers are mainly preferred for gasification of hard coals.

1.3 ZONES OF GASIFIER

In a gasifier, the carbonaceous material undergoes gasification process in different processes or zones. These different zones of gasifier are named as drying, pyrolysis, combustion and gasification zone. Regardless of the noticeable overlap between each zone, due to the different thermo-chemical reactions these processes are considered to be in

different zones. Zones of gasification process in a downdraft biomass gasifier are shown in Figure 1.3.

Drying Zone: Drying zone is the zone in which the biomass first comes in contact with the gasifier. The main process in this zone is dehydration or the removal of moisture which is fundamentally a mass transfer operation. Biomass feedstock has moisture ranging from 5 to 55%. Typically dehydration occurs at the temperature above 100°C, where the moisture is removed and converted to steam. This moisture is removed due to more conduction and less convection that is generated from the bottom zones in the gasifier, without undergoing any decomposition or chemical reaction.

Pyrolysis Zone: Pyrolysis or devolatilization is the process in which feedstock undergoes thermal decomposition in the absence of air/oxygen. The irreversible devolatilization reaction is the main reaction taking place in this zone in temperature ranging from 200°C to 500°C [18]. Energy required for pyrolysis is obtained from the combustion zone where the exothermic reactions happen. The products of devolatilization process are volatiles along with char, tar resulting in about 85% weight loss of feedstock. The volatiles released in this zone are the mixture of gases like H₂, CO, CH₄, H₂O, and CO₂ along with black corrosive liquid tar, whereas chars are the solid carbon residue. The tars and char will further have to undergo decomposition partial reduction in the combustion and gasification zones. The pyrolysis and tar cracking reactions are as follows where primary tar can be expressed as C_{6.407}H_{11.454}O_{3.482} and secondary tar can be mainly assumed as benzene [19].

Volatile \longrightarrow 0.268CO + 0.295CO₂ + 0.094CH₄ + 0.5H₂ + 0.255H₂O + 0.004NH₃ + 0.2primary tar

Primary tar \longrightarrow 0.261secondary tar + 2.6CO 0.441CO₂ + 0.983CH₄ + 2.161H₂ + 0.408C₂H₄

Oxidation/Combustion Zone: The combustion/oxidation zone supplies the energy for the subsequent gasification reactions. All the oxidation reactions are exothermic in nature and yield the temperature ranging from 800°C to 1100°C. In this zone the carbon present in volatiles and chars formed from the devolatilization reaction reacts with oxygen in air to form carbon dioxide as per the following reaction.

$$C + O_2 \rightarrow CO_2$$
 $\Delta H = -393.5 \text{KJ/mol}$

Whereas the Hydrogen and methane reacts with oxygen to produce steam or water vapor and carbon monoxide respectively whose reaction is as follows:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$
 $\Delta H = -242 \text{ KJ/mol}$

$$CH_4 + 1.5 O_2 \rightarrow CO + 2H_2O \quad \Delta H = -110 \text{ KJ/mol} \quad [20]$$

Reduction/Gasification Zone: In the reduction zone, a number of high temperature chemical reactions between different gaseous and solid reactants take place in the absence of oxygen. In general, the produced carbon dioxide, water vapor partially combusted volatiles and chars from above zones pass through the porous red hot charcoal bed resting above the grate to undergo reduction. The major reactions taking place in this zone are water gas reaction and the bouldouard reactions. The solid carbon left in this zone red hot with all the volatile matters driven off and the temperature in this zone is in between 650°C and 900°C. The reduction reactions in this zone are mentioned below [3],[20]:

Water gas reaction:
$$C + H_2O \rightarrow CO + H_2$$
 $\Delta H = +118.5 \text{ KJ/mol}$

Water shift reaction:
$$CO + H_2O \rightarrow CO_2 + H_2$$
 $\Delta H = -40.9 \text{ KJ/mol}$

Bouldouard reaction:
$$C + CO_2 \rightarrow 2CO$$
 $\Delta H = +159.9 \text{ KJ/mol}$

1.4 PRODUCT OF GASIFICATION

Gasification process produces syngas and/or producer gas along with bio-oil, char and ash [21]. Produced combustible gas is a mixture of gases produced by the gasification or incomplete combustion of carbonaceous material such as biomass. The syngas consists of carbon monoxide, hydrogen and small quantities of carbon dioxide. Similar to syngas, if the gasification product has an extent of hydrocarbons link methane, CO, H₂ along with significant amounts of non-combustibles such as carbon dioxide and nitrogen from the air then that mixture is referred as producer gas [22].

1.5 APPLICATIONS OF GASIFICATION

The production of syngas as a renewable energy source has many advantages as it being ecologically benign in nature. Due to the depletion of non-renewable sources and its replacement with biomass as an energy source, gasification processes has gained a huge attention in the recent times.

Syngas is a product of gasification and the main applications are a) Fischer Tropsch process to produce diesel or to be used as a catalyst, b) Electricity generation, c) Production of ammonia & methanol, d) Hydrogen for refineries etc. [21]. The capacity of the major applications of gasification processes is shown in Figure 1.5. Of all the major applications of gasification, the electricity generation and Fischer Tropsch process contributes to nearly about 50%. The generation of electricity from gasification gained a lot of significance in late 90's. The heat produced when burning the syngas is used to evaporate water to make supersaturated steam, which is sent to turbine to generate electricity.

According to the US Department of Energy, in 2009, the potential of biomass usage in electricity generation is projected to be 22 GW by the year 2022 [23].

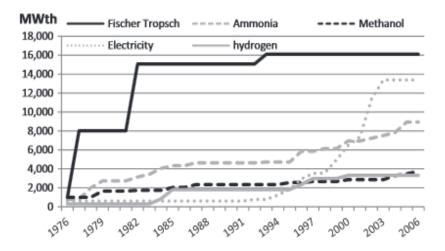


Figure 1.5. Accumulated capacity of main applications of gasification

The Fischer Tropsch is the catalytic conversion of carbonaceous materials such as biomass, coal to produce fuels from synthesis gas. The Fischer Tropsch application to gasification process has gained a lot of importance to meet the energy demands and environmental regulations in the modern world. In this process, the syngas produced from the gasification of biomass is cleaned to remove impurities and subjected to Fischer Tropsch catalytic reactor to produce clean biofuels. Due to its various applications and advantages, there has been an increasing interest in research and development of biomass gasification processes, to improve the economic and technical issues to cope with depleting fossil fuels.

2. DESIGN AND FABRICATION

The design and fabrication of the down draft biomass gasifier to produce Syngas, is one of the main objective of this paper. The design is divided primarily into three divisions namely, fixed bed reactor, transport line and the combustion flare. The material that was used to design the reactor and combustion flare are carbon steel and black iron for transportation unit. Gasifier is shown in Figure 2.1.

2.1 REACTOR

The down-draft fixed bed reactor has three encircled plenums with increasing diameter namely reactor core, air plenum and syngas plenum respectively. After a few experimental investigations, the air plenum was removed from the design, as the amount of air supplied into the reactor and how to control that, plays an important role during the gasification process.

2.1.1 Reactor Core. The reactor core is the inner most cylinder with an internal diameter of 8" and a height of 19". The biomass feedstock fed from the top is gradually passing through the distinguishable steps of drying, pyrolysis, combustion and gasification zones inside this reactor, to undergo a thermo-chemical conversion. A perforated, iron grate is set up at the bottom of this cylinder to support the biomass bed and also to dispose the ash continuously, avoiding ash sintering that was generated during the gasification process.

Sixteen air nozzles at four different levels as shown in Figure 2.3 are arranged to support the combustion of biomass where is desired. These nozzles are arranged in such a way that there are only one 2", one 4" and two 3" nozzles along a cross section, as well as vertically in a column; besides, they are arranged alternatively at an angle of 60° and 120° to render uniform air distribution throughout the whole cross section of a cylinder.

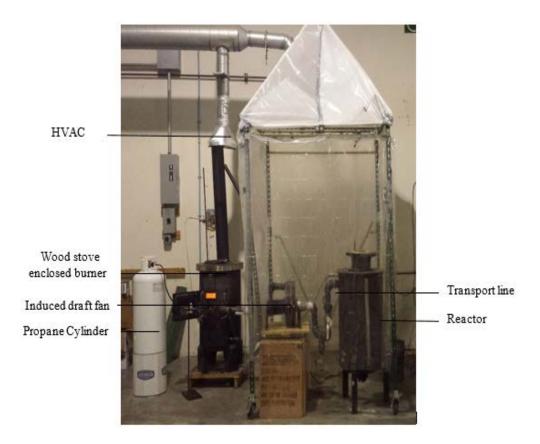


Figure 2.1. Downdraft biomass gasifier unit



Figure 2.2. Reactor core with a) Air nozzles and b) Thermocouple openings

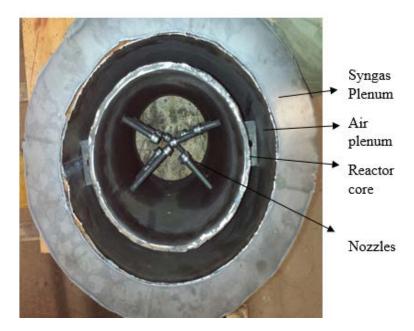


Figure 2.3. Assembly of air plenum and reactor core

The woody biomass feedstock is fed to the conveyer at a desired speed which loads the feed to the hopper. The top of the reactor core has a flange of 8" to which the hopper is mounted. The hopper has a gate valve at the bottom which on opening allows the feed in to the reactor while controlling the feed rate.

2.1.2 Air Plenum. The reactor core is surrounded by the air plenum of 12" in diameter and 19" in height. Air enters the reactor core through the nozzles connected to air plenum. After certain experimental investigations, it was decided to close the air plenum and let the air flow free from the reactor's top opening. The reasons being a) To avoid rapid heat loss in the reactor core surrounded by cold air plenum, b) To avoid bridging inside the reactor by cutting out the nozzles. In the latter model air plenum was closed and the nozzles were removed since the biomass feedstock such as picks and flakes block the reactor as the feed flows down. Figure 2.3 shows the reactor core with nozzles and air plenum.

2.1.3 Syngas Plenum. Air plenum is surrounded by Syngas plenum which has 20" diameter and 36" length; Syngas plenum is covered by a donut shaped carbon steel plate. Syngas evolved inside reactor core is pulled into Syngas plenum through reactor bottom and exits to Syngas outlet which is at the depth of 4.5" from the top of reactor. The Ash generated is collected from the opening in the cup shaped dome present at the bottom of the syngas plenum. Gasifier effluent flowing out from syngas plenum enters the "Tarcollection" unit after the syngas outlet.

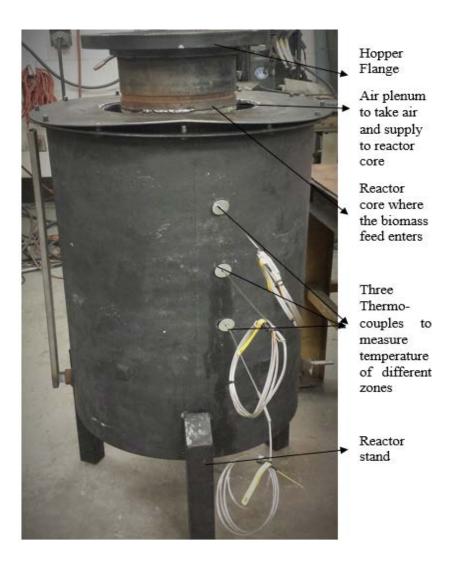


Figure 2.4. Assembly of reactor core, air plenum and Syngas plenum

The reactor is fitted with 8" flange on the top, to mount a hopper to supply continuous feed; also the top portion of the reactor has a small opening to purge the nitrogen during the shutdown process to kill the ongoing reactions. The thermal profiles of the reactor are monitored on LabVIEW using three thermocouples placed inside the reactor as shown in Figure 2.4. These three thermocouples are inserted at the height of 2", 7.5" and 13" from the bottom of reactor core thus obtaining the temperatures of different zones. The top thermocouple measures the temperature of drying zone where the temperature is around 150-200°F followed by combustion and gasification zones indicating 1800°F and 1400°F respectively for the middle and bottom thermocouples.

2.2 CONDENSATION SYSTEM

A U-shape transportation line of 2" ID is connected to the syngas outlet followed by an induced draft fan of 1hp, to suck the gas produced in the reactor. As shown in Figure 2.4, the transportation line is equipped with a coiled tube which acts as a condensation unit to cool down the produced gas and has two valves at the bottom to collect the bio-oil that is produced. In addition a liquid trap is present after the condensation unit to release any pressure and avoid puffing as an additional safety measure.

An upstream ball valve is installed before the fan, to control the flow through the whole transportation system starting with a setting of 0 when fully closed to 8 when fully open. For steady state operation valve is set between 2 and 3. Table 2.1 below shows the velocity and flow rate of the gas at each valve setting. In the downstream flow after the induced fan, a T-junction is connected using a valve to take sample of produced gas and find the composition. This valve is closed when not in use leading all the flow to the

combustion flare. The components in condensation unit before entering the combustion flare are shown in Figure 2.5.

The condensation unit has three thermocouples attached to the control system giving the temperatures of syngas out, fan in and fan out, respectively. Additionally, two oxygen sensors are placed one right after the syngas outlet from reactor and another before the combustion chamber to measure the concentration of oxygen in the system and make sure it is always below 1% to avoid explosion and ensure there is no leak in the system. This means that the mixture of syngas and air inside the reactor and piping system is always too rich to burn which means there is not enough air or oxygen for the combustion to happen. A quick look at the upper and lower flammable limit of hydrogen (75% - 4%), carbon monoxide (75% - 12%), and methane (15% - 5%) shows us having 1% oxygen by volume in the mixture will always keep us in the safe zone. Oxygen sensors are always monitored and recorded for safety reasons and to run the system effectively.

2.3 COMBUSTION FLARE

As shown in Figure 2.1, in the initial experiments the woodstove was used as an enclosed burner to burn the produced syngas. Later, an enclosed combustion chamber was built which is a cylinder is made of carbon steel with 24" diameter and 44" in total height. The condensation unit is connected to this chamber through an opening of 2" diameter on the bottom; besides the bottom of enclosed combustor has 8 holes round it, which supplies the oxygen required for syngas combustion. There is also an inlet opening for a round propane burner at the height of 6" from bottom as well as a window on the top to observe the flame. A camera is placed outside of this window to monitor and record the flame as shown in the Figure 2.6.

Table 2.1. Velocity and flow of gas at different valve opening

Valve Setting	Velocity (ft/min)	Flow (ft ³ /min)
Setting 8	3170	69.15
Setting 7	3130	68.28
Setting 6	2130	46.46
Setting 5	1580	34.46
Setting 4	1150	25.08
Setting 3	680	14.83
Setting 2	320	6.98
Setting 1	25	0.545
Setting 0	0	0



Figure 2.5. Complete gasifier system

To avoid heating the ground, the bottom of the combustion chamber is insulated with glass cotton, covered by a thin metal plate and gravel of 2" depth on the top. The whole body of the chamber is also insulated from inside to avoid having a very hot external surface which would be considered a safety issue. Inside view of the combustion flare is shown in Figure 2.7. Spark ignition is used to ignite propane burner operated during the startup and this flame is utilized as a source of kindle to burn the syngas produced from gasification. A thermocouple is placed at the top of the combustion flare to monitor the temperature of exhaust gas going to the HVAC unit.



Figure 2.6. Combustion flare showing camera, window flame and air holes



Figure 2.7. Top view of combustion chamber showing insulation, ring burner and syngas outlet opening

3. METHODOLOGY

3.1 BIOMASS FEEDSTOCK CHARACTERISTICS

A feedstock in general is defined as a raw material that requires some processing to convert one form of matter to some other useful form of matter. Biomass feedstock is a biologic material derived from the living organisms which can be used as a fuel, directly or indirectly. The various sources of biomass are in concordant to the ecosystems from which it is obtained. The type of feed which is used as a fuel in the designed down-draft biomass gasifier is the woody source of biomass. The experiment is conducted for three different feeds such as picks, pellets and flakes to compare the heating value and the amount of syngas produced.



Figure 3.1. Left to Right: Pellets, Flakes and Chips

As shown in Figure 3.1, the wood picks are the unprocessed woody biomass obtained from Canadian forest which have average size of 0.5 in, whereas the flakes and pellets are approximately the same size processed feed to increase effectiveness and transportability. Flakes are the processed wood in which the bark is removed first and cut into small uniform sizes whereas wood pellets are generally made from compacting saw dust in uniform sizes.

The chemical and physical properties of biomass fuels determine the design and performance of a reactor; besides the components of the producer gas. Five samples of each feedstock shown in Figure 3.1 were taken randomly and tested for proximate and ultimate analysis by using thermogravimetric analyzer and CHN elemental analyzer respectively to get the comprehensive details of the biomass feed. These analyses were carried out on dry basis for which the feedstock samples are dried in a vacuum oven for nearly 8 hours at the temperature of 300°F. The average proximate ultimate analysis and heating values of all the feedstocks are shown in Table 3.1, Table 3.2 and Table 3.3 respectively.

Table 3.1. Proximate analysis of all feedstock

	Picks	Flakes	Pellets
Moisture %	35.19	11.01	7.56
Volatile dry %	82.28	86.15	87.23
Fixed Carbon dry %	17.26	13.32	12.39
Ash dry %	0.46	0.53	0.38

Table 3.2. Ultimate analysis of all feedstock

	Picks	Flakes	Pellets
Carbon %	48.81	48.24	49.03
Hydrogen %	5.96	6.15	5.58
Oxygen %	44.98	45.55	45.33
Nitrogen %	0.26	0.06	0.06

Table 3.3. Heating value of all feedstock

Heating value	Picks	Flakes	Pellets
Cal/gm	4509.90	4562.12	4621.76
Btu/lb	8117.82	8211.82	8319.16

The angle of repose or the critical angle of repose of a granular material is the steepest angle of descent or dip relative to the horizontal plane to which a material can be piled without slumping. At this angle, the material on the slope face is on the verge of sliding. The angle of repose can range from 0° to 90°. Smooth, rounded sand grains cannot be piled as steeply as can rough, interlocking sands.

When bulk granular materials are poured onto a horizontal surface, a conical pile will form. The internal angle between the surface of the pile and the horizontal surface is known as the angle of repose and is related to the density, surface area and shapes of the particles, and the coefficient of friction of the material. However, the angle of repose is also gravity-dependent. Material with a low angle of repose forms flatter piles than material

with a high angle of repose. This becomes very important inside a gasifier where you have a pile of biomass on the top of a flat plate. The flatter piles result in a better heat transfer and more stable combustion bed.

3.2 EXPERIMENTAL METHOD

The experiments are conducted in a designed down draft fixed bed biomass gasifier system where the major components being the reactor and combustion flare. It took us along time (4 months) and carrying several experiments using different types of biomass as feedstock, to develop an effective operating procedure along with its safety protective measures. A sample of produced syngas was essayed to GC to acquire the composition of chemical species in the produced gas. In better understanding, the test procedure is divided into three stages namely a) Start up, b) Steady state continuous and c) Shut down process. Before we start discussing the test procedure, a hazard and operability study (HAZOP) is discussed first in section below.

3.2.1 Hazard and Operability Study (HAZOP). A hazard and operability study (HAZOP) is a structured and systematic examination of a planned or existing process or operation in order to identify and evaluate problems that may represent risks to personnel or equipment, or prevent efficient operation; it is carried out by a suitably experienced multi-disciplinary team (HAZOP team) during a set of meetings. The HAZOP technique is qualitative, and aims to stimulate the imagination of participants to identify potential hazards and operability problems; structure and completeness are given by using guideword prompts.

In this study, the whole system was divided to separate sub-systems including reactor core, air injectors, air plenum, syngas plenum, tar trap, ID fan, solid char removal,

transport line, sampling branch and enclosed combustion chamber. For each sub-system, numbers of possible cases were discussed which could lead to a dangerous situation. The cause and consequence of each case was investigated and also it was recommended how to control or avoid these kinds of situations. A copy of final HAZOP spreadsheet was prepared and signed by the operators and people from department of environmental health and safety who participated in meetings and reviewed the whole final result.

3.2.2 Start Up. Before starting the experiment it has to make sure that all the safety standards are met. Cameras and the other recording systems are monitored using the LabVIEW, which is primarily used for data acquisition. For startup, initially the condensation unit is turned on by opening the water valve which is kept open throughout the experiment to condense the hot gas produced. Later the combustion flare is preheated for about 15 minutes by kindling the burner with the propane. This is exercised to provide an igniting source to the syngas entering the combustion chamber through the downstream valve. Meanwhile, the fan is turned on and a 1 inch ball valve and the tar/bio-oil collecting jar are placed at the bottom of cooling section.

The experiment is started by loading approximately 10 lb. of biomass feed into the reactor core and burning it for about 15 minutes. While the biomass is burning the upstream valve which controls the fan speed is set to 3 to pull the produced gas and smoke out of reactor and push it to the combustion flare. As the reaction proceeds, the temperature starts increasing to 1600-1800°F in combustion zone; At the same time both the oxygen sensors show approximately same valve in a range of 0.6-0.8% ensuing be always under UFL of hydrogen and carbon monoxide and also no leaking in the system. Remaining ash at the

bottom of reactor core falls down through the ash grate. As the biomass bed moves downward the vibrator is turned on to help the flow and avoid bridging inside the reactor.

3.2.3 Steady State Continuous Procedure. Approximately 4-8 lb of new batch of feed, depends on the type of feed, is fed when the combustion bed is stablished. As the feed is fed, the temperature profiles of all zones starts decreasing immediately because the added feed is of room temperature and has moisture and increases again to attain a steady state profiles for combustion and gasification zones. As the reaction proceeds, a perforated plate is kept on the top of the reactor to limit the supply of oxygen. During the steady state process, the gasification zone is just above the ash grate (2" from the bottom) and shows a temperature of 1400°F in the bottom thermocouple. Simultaneously the combustion zone is maintained just above the gasification zone approximately at the length of 5-8" from the bottom of the reactor core. The combustion temperature is shown by the second thermocouple which is movable so that the thickness of the combustion bed can be known which is approximately 2-4 inches. After repeated procedures, this method is found out as the effective method to avoid piling up of solid residues in the gasifier by leaving some amounts of biomass left unburnt. Usually the biomass combustion zone is present at the temperature of 1600-1800°F at the while the upstream valve is set at 3. By opening the upstream valve, suction side flow rate goes up, resulting in pulling more air into combustion bed and increasing the corresponding temperature; the bed moves down and vice versa.

As the bed goes down a new pile of feed is added to the reactor and the above procedure is repeated for the steady state process. The biomass is being processed approximately at a rate of 0.5 to 1.5 lb. per minute in this reactor. The oxygen sensors are

maintained at the level below 1% and approximately same for both sensors and other recordings are constantly monitored in the LabVIEW throughout the procedure to ensure safety of the system. When the gasifier is running at a steady state with the combustion temperature of around 1600-1800°F, samples of gas will be taken through a sampling branch before entering the combustion chamber. After the gas is collected the gas sampling valve is set back to close and the gas is being tested in the GC (gas chromatograph) to find the composition of produced gas.

3.2.4 Shutdown Process. Top of the reactor will be sealed during this step to avoid air flow into the reactor and nitrogen is purged through the nitrogen purge valve until the gasification reactions are killed. Having the induced fan turned off and purging the nitrogen simultaneously, the temperature in combustion and gasification zones decrease rapidly and settles down slowly after a while. By closing the upstream valve and sealing the top of the reactor, the whole gasifier will be isolated from the transportation pipe and combustion chamber, and absolutely no air/gas is going to or coming out of the reactor. Inside the gasifier, reactor core is trapped by nitrogen which results in shutting down all the reactions in combustion and gasification zones. The propane tank and the condensation unit are turned off after the reaction is killed in the reactor. It takes approximately 3-5 hours (depends on the type of biomass and the duration of purging nitrogen) to get the temperatures back to the room temperature. After this the char in the reactor is vacuumed and the tar collecting jar is removed from cooling system.

4. RESULT AND DISCUSSION

The experiments were conducted for wood chips, flakes and pellets in the designed down draft biomass gasifier. The optimum operating conditions for the three feeds used in this study is different because of their composition and transportability of the feed. The following section discusses the various effects that were caused while conducting the experiments.

4.1 PELLETS

As discussed in the methodology section, some amount of pellets was used for startup process. The k-type thermocouples and oxygen sensors present in the reactor, records the values for every 4 seconds. Pellets which are generally made from compacted sawdust, has less moisture content, high heating values and also high transportability without causing any bridging or voids along the bed, as compared to wood chips and flakes.

They also catch fire immediately and produce a high quality syngas which is transported through the fan to the combustion flare. For pellets, if the upstream valve is opened too much i.e. a very high flow of air into the reactor, then the temperature of combustion zone increases and vice versa. Too much increase in flow of air is also not recommended as it results in combustion than gasifying the feedstock. Another important factor which effects the flow of air into the reactor is the height of fresh biomass bed exist on the top of combustion zone as a restriction to air flow. i.e. if there is just a small amount of fresh feed on the top of the bed, then the air flow into the reactor is high which finally results in complete combustion of feedstock; and if there is too much feed above the combustion bed, it will block the air to go to combustion bed which might result in losing the bed. The amount of air that is entering the reactor is controlled by the upstream valve

on the suction side of the induced draft fan. Also the concentration of oxygen is always monitored and recorded to make sure the system is always kept below 1% which is much lower than the UFL in this case.

Whenever a new feed is added to the reactor during steady state process the temperatures profiles of drying, combustion and gasification zone decrease initially because of the cold temperature of the feed (75°F) compared to the combustion bed temperature (1700°F) and also releasing the moisture of the new feed in drying zone which will be pulled down through the bed, and gains back to the steady state combustion and gasification temperatures of around 1700°F and 1400°F respectively as shown in Figure 4.1.

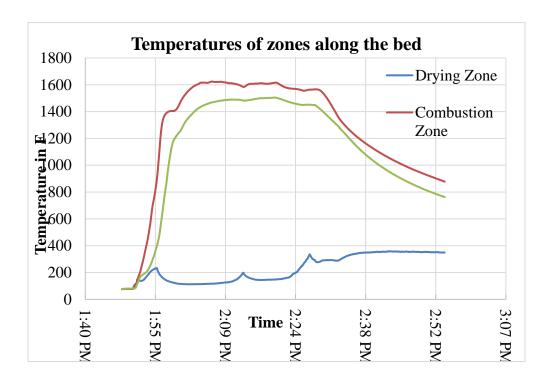


Figure 4.1. Temperature profiles of zones along the bed for pellets

As shown in Figure 4.1 the experiment was started at 1:50 pm by lighting the top surface of pellets bed. The upstream valve is set at 3 which is equivalent to 14.83 ft³/min of flow inside the transportation pipeline. Immediately the temperature of all three zones inside the reactor shoots up. Before we add any new feed on the top of reactor, it has to be made sure that a well-established combustion bed is present. Temperature is a key parameter is used to find out if the combustion and gasification bed are ready to receive a new pile of feed. Usually 1400°F for combustion and 1200°F for gasification are the good temperatures to start feeding the reactor. At 1:56 pm, when the desired temperatures are achieved, a new pile of raw feed is added to the reactor. Since the new feed is at room temperature and has moisture, there is a change in slope of both combustion and gasification profiles also making a temperature drop in drying zone. After 4 minutes temperature in reaction zones start going back up to steady state.

During steady state process, drying zone temperature also indicates when a new feed should be added. The drying zone temperature starts going up gradually as the biomass bed moves down and leaving a large void space above the combustion bed resulting in heat convection from combustion to drying zone. This means that the previous pile of feed is almost processed and now it's a good time for adding the new feed. So based on this observation, at 2:13 pm a new pile of feed is added and again a temperature drop is observed in all zones inside the reactor. Shut down process is started at 2:26pm by purging nitrogen into the reactor and sealing the top opening using a knife valve. At this time, the combustion and gasification reactions are killed resulting in a dramatic temperature drop in above mentioned zones. At 2:32 pm the temperature in drying zone starts going up and

this only because of the conduction heat transfer from the reactor wall to the thermocouple as long as the other two temperature profiles are going down.

Other important factors that are affected inside the system are Syngas outlet from syngas chamber, Fan inlet and Fan outlet temperatures. As combustion bed increases due to increase in air flow, the temperatures of syngas outlet raises inside the reactor and vice versa. So the condensation unit must be effective to cool down the hot gas before passing through the fan and remove the moisture and bio-oil present in stream of produced gas. Temperatures profiles of syngas outlet, Fan inlet and Fan outlet are shown in Figure 4.2. The temperature of syngas leaving the reactor is in direct relation to the upstream valve setting (i.e. air flow into the reactor system) which itself is in direct relation to the gasification and combustion zone temperatures. The temperature of syngas outlet has to be controlled before it goes to the fan to avoid melting of blades and damaging the fan. This could be done by controlling the upstream valve setting. For example, at time 2:20 pm the temperature of syngas outlet has reached 400°F then the valve setting is changed from 3 to 2.5 which resulted in a temperature backdrop to 360°F, as shown in Figure 4.2. During the shutdown process, temperature of syngas outlet decreases drastically along with the temperature inside the reactor which is clearly evident at time 2:26pm.

So during steady state process care has to be taken that the raw feed on the top of combustion bed has to be maintained in optimum amounts so that there is not either a large temperature drops for various zones insides the reactor or a very high flow of air into the bed resulting a shift from gasification process to complete combustion.

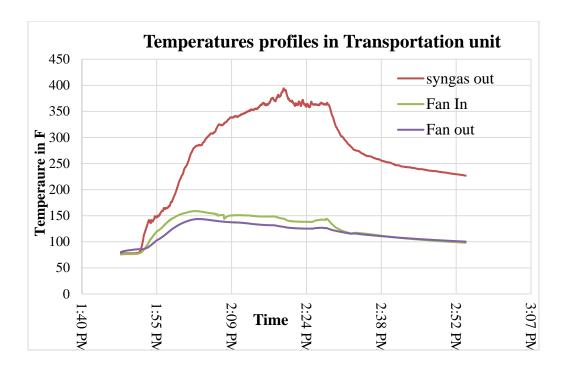


Figure 4.2. Temperature profiles in the transportation unit for pellets

Nitrogen purge is stopped after we make sure that the reaction inside the reactor is killed. Figures 4.3 and 4.4 show the complete profile of startup, steady state and shut down mode of temperatures inside the reactor and transportation unit respectively. After reactions are killed the by nitrogen purge the system is left to cool down on its own.

Figure 4.5 below shows the oxygen sensor vs time plot, in which before time 1:50 pm, both the oxygen sensors are showing AFR nearly 8 which is equivalent to 21% oxygen. When the experiment starts at 1:50 pm, both these values go down very quickly showing less than 1% of oxygen concentration in the exhaust gas, coming out from the reactor. This concentration should always be maintained below 1% during the whole procedure to make sure that the process is always below UFL of H₂ and CO.

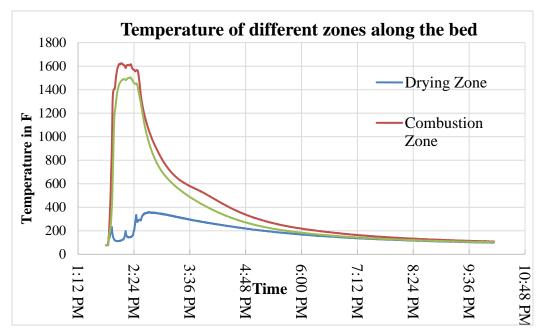


Figure 4.3. Temperature profiles of zones inside the reactor for pellets

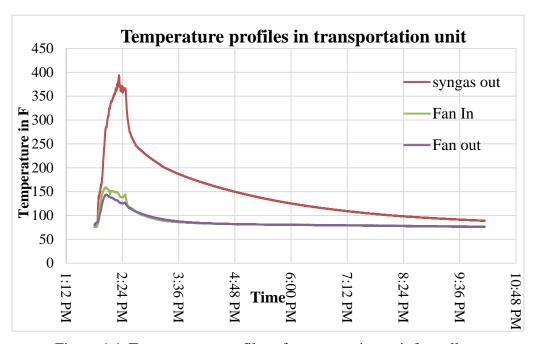


Figure 4.4. Temperatures profiles of transportation unit for pellets

During the shutdown process, the upstream valve is kept completely closed to isolate the reactor from the fan and combustion chamber to avoid air flow into the reactor. At this time, there is neither a gas leaving nor air entering the reactor. So, the syngas oxygen values stays the same for a long which gives us an assurance that the reaction inside the bed is not going to start again since there is no air. After a while it increases very slowly over time and this is because of imperfect sealing of knife valve over the top opening. On the other hand the downstream oxygen sensor (burner oxygen), the one close to combustion chamber, starts going up immediately after closing the valve. It definitely shows the flow of air into downstream pipeline because of negative pressure created by the HVAC system at the top of combustion flare.

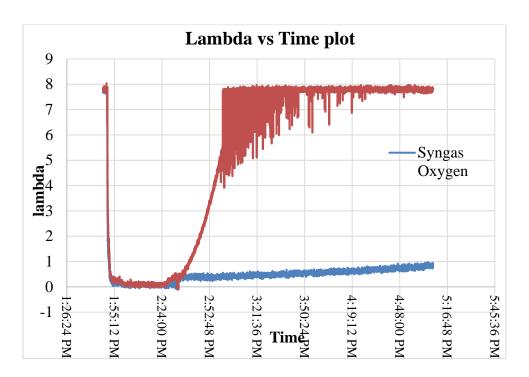


Figure 4.5. Plot of oxygen sensor lambda values vs Time for pellets

4.2 FLAKES

Flakes or wood shavings are also the processed biomass with slightly higher moisture content compared to pellets. The flow of flakes inside the reactor is much less compared to pellets which means they hardly move down along the reactor. A vibrator is used to assist moving the bed down while processing flakes. Since flakes have much lower density than the other two feed stocks in this study, they are being gasified much slower in terms of mass rate. This is not be confused with the rate of burning of flakes in terms of volume which is a lot faster than pellets and picks. They also follow the same procedure and trends that were followed while processing of pellets. A slightly higher amount of air is required to support combustion so that the combustion and gasification temperatures are in the desired range.

Optimum fresh biomass bed on top of combustion bed should be maintained to run a continuous steady state process by not increasing the syngas outlet, Fan in and Fan out temperatures. During the shutdown process, the reaction is killed by purging the nitrogen and cools down to the room temperature quicker than pellets. Figure 4.6 below are the temperature profiles that are inside the reactor.

When combustion and gasification temperatures are high, it increases the syngas outlet temperature which results in adjusting of the valve setting or to decrease the air flow into the reactor same as described for pellets. Syngas outlet is usually kept below 500°F so that the condensation unit is able to cool it down below 200°F before entering the fan. The temperature profiles in transportation line are shown in Figure 4.7. The oxygen sensor values when processing the flakes shown in Figure 4.8 are slightly more when compared to pellets and wood chips because of the porosity inside the bed for flakes.

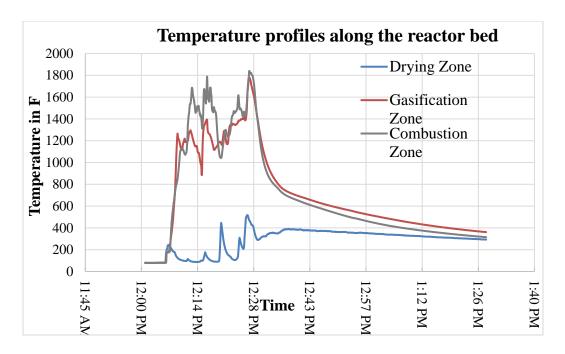


Figure 4.6. Temperature vs time profiles inside the reactor for flakes

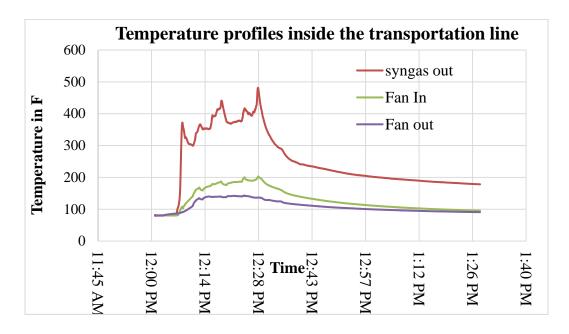


Figure 4.7. Temperatures profiles in transportation unit for Flakes

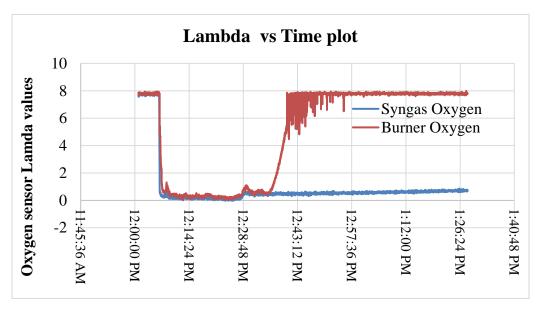


Figure 4.8. Lambda vs Time for Flakes

4.3 WOOD CHIPS

Wood chips having nearly 35% moisture, it is difficult to start up the experiment except get dried first. So wood pellets are used for startup and wood chips would be added once a good combustion bed with pellets has been formed. Wood chips too follow the same operating procedure and patterns such as pellets and flakes, but care should be taken that there is a probability of forming larger number of voids in the biomass bed. Since in flakes and picks, the combustion bed does not tend to spread uniformly along the cross section and instead makes voids and holes inside the bed. So a good shaking or stirring system is required to avoid the above said issue. Figure 4.9 shows the graph of temperature profiles inside the reactor. In the graph the first 1 hour of the experiment was for pellets and the drop of combustion and temperatures profiles is due to the addition of feed, while in the latter part of the experiment wood chips were added. The drop in the combustion and gasification temperature profiles when new pile of wood chips were added is more than

compared to pellets because of the high moisture content of chips. So a very low feed rate of wood chips are added to the reactor to make sure the temperature drop in combustion, gasification beds are low and to maintain a stable steady state process. Figure 4.10 shows the temperature profiles of Syngas out, Fan in and Fan out. Also, the flame inside the combustion chamber for wood chips is less dense and stable compared to pellets because of the low heating values and high moisture contents of wood chips.

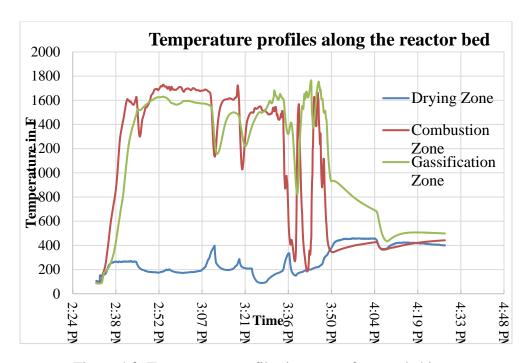


Figure 4.9. Temperature profiles in reactor for wood chips

Figure 4.11 below shows the plot of lambda vs time plot for the oxygen sensors which follows the same trend as discussed for pellets. Before 3:50 pm the process was in progress where the oxygen concentration should be below 1%. At 3:50 pm, the shutdown process starts and there is a raise in downstream oxygen sensor values (burner oxygen) due

to the negative pressure of HVAC unit as discussed for pellets, but around 4:10 pm there is a sudden drop in this values and it goes back up.

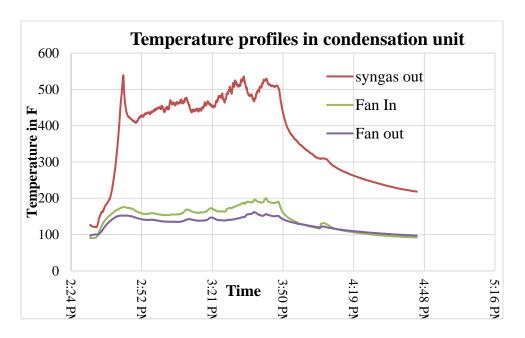


Figure 4.10. Temperature vs time profiles in condensation unit for wood chips

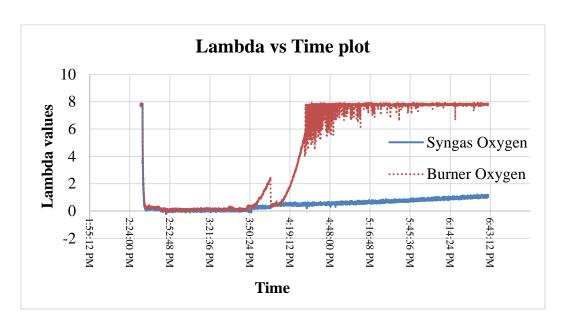


Figure 4.11. Plot of Lambda vs Time for Woodchips

In Figure 4.9, it was clearly seen that the temperature of combustion and gasification zone increased which resulted in purging nitrogen again.

4.4 SYNGAS COMPOSITION

The composition of syngas produced from this biomass gasification process is shown in Table 4.1 where air was used as gasification medium.

Table 4.1. Syngas composition using air as gasification medium

Component	Vol %
Hydrogen	18
Carbon Monoxide	21
Carbon Dioxide	16
Methane	2
C ₂ ⁺ Hydrocarbons	2
Nitrogen	41

4.5 BIO-OIL/TAR

Bio-oil is the dark color liquid fuel formed as a side product of pyrolysis reaction. In the pyrolysis reaction, carbonaceous biomass feedstock undergoes thermal degradation to form volatiles, char, gases and ash. These volatiles when condenses, forms a brownish black thick liquid known as wood oil or bio-oil. It has significant amounts of miscible water i.e. 20-30% water depending upon the moisture contents in the biomass feedstocks. The quality and composition of this bio-oil also rely on the type of pyrolysis that took place and on the composition of feedstock. Like Biomass, bio-oil is also more environmental friendly

fuel with less CO₂ and SO₂ emissions and has nearly 40% lower heating values compared to fossil fuels. Figure 4.12 below shows the picture of bio-oil that was collected during the process [18],[24,[25].



Figure 4.12. Bio-oil produced during the pyrolysis process

5. CONCLUSION AND FUTURE WORK

The gasification process of various biomass feedstocks (wood chips, pellets and flakes) are studied in the designed downdraft biomass gasifier. The biomass bed and condensation unit temperatures correlated with time were discussed. Pellets having high density and high calorific values compared to chips and flakes which produces a more stable and dense flame than the other two feed.

The important point that is learnt is that, the feed rate and flow of air to the reactor play an important role for a steady state process. So an optimum level of feed and air need to be sent to the reactor to retain the steady state conditions. When the feed rate is high, the air that has to be flown into the reactor is also high, which sometimes may result in just combustion than gasification. It is also discussed how the feeds are different in terms of rate of burning and gasifying. Stability of the bed was compared as well and as a conclusion, pellets were better than picks better than flakes. It was also observed that pellets have better flame than flakes better than picks.

For future work, it is suggested to mix the flakes that have low moisture with picks with high moisture to decrease the total moisture of the feed and also help the flow of flake inside the reactor. Also it is recommended to chop, dry and pelletize the flakes and picks before sending those in and compared the stability of the bed and the flame inside the burner to the pellets again.

A scaling project is planned which includes changing the reactor core size down to 4 in and up to 12 in diameter instead of the existing 8 in and find out the effect of this change on the rate of production of syngas which is believed not going to be linear. Also the change in temperature profiles along the bed and possibility of having a stable,

consistent and uniform combustion bed in a very large diameter reactor will be studied.

Definitely the change in the amount of heat loss will be studied too since the surface area to volume ratio will change when the reactor diameter is changed while keeping the same length.

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IV. MULTIZONAL MODELING OF BIOMASS GASIFICATION USING ASPEN SIMULATION

ABSTRACT

To meet the demand of increasing energy needs, our current focus is on commercially developing biomass gasification process. Efforts to improve process yield for commercial operation relies on first developing a complete Aspen based process model, identifying the key process parameters for the reactor and then optimizing the overall process. The proposed model is designed to simulate a real biomass gasification system that was designed and built here in MS&T at steady state along with a detailed modeling of all four zones in this downdraft gasifier including drying, pyrolysis, combustion and gasification zone. The model can easily be modified for different operating facilities and conditions.

The current model will analyze the following important aspects: Syngas produced, Tar present in the syngas, Equivalence ratio (air/fuel) and temperature profile in the system. All reactors describing different processes inside the gasifier are kinetically modeled in a CSTR with surface and volumetric reactions. ASPEN process parameters were identified to match different operating factors and used to optimize the complete process. Results are verified with experimental yield data collected from lab scale biomass gasifier operated by Missouri S&T Energy R&D Center.

1. INTRODUCTION AND BACKGROUND

Today, the world is looking for renewable sources of energy. Global oil prices have fallen which has led to a downfall in oil & gas industry in United States. This has made us realize the importance of obtaining energy from bio-based products. Converting solid biomass into a mixture of gases which mainly consists of carbon mono-oxide and hydrogen known as syngas by thermochemical process is called biomass gasification. Recovering energy from waste by gasification process is a cost effective and reliable process and provides clean fuel. Currently biomass covers approximately 10 percent of the global energy supply [1].

Among renewable resources, the most important ones were biomass and renewable waste accounting for just under two thirds (64.2%) [2]. In 2009 about 13% of consumed biomass was to generate heat and power, while the industrial sector consumed 15% and transportation 4% [1]. Shares of energy sources in total global primary energy supply in 2008 is shown in Figure 1.1 [3].

Three general pathways to produce energy from biomass are shown in Figure 1.2 [4]. Our focus is on thermo-chemical process as it can handle various types of biomass. Amongst the thermo-chemical conversion technologies, biomass gasification has attracted the highest interest as it offers higher efficiencies in relation to combustion [5].

Gasification of biomass is primarily done in fixed and fluidized beds. The fixed bed gasifiers are suitable for small-scale applications. Our model is based on a fixed bed downdraft reactor which is being run at Missouri S&T. Aspen Model of biomass gasifier is used to evaluate the effect of operating parameters & feed conditions.

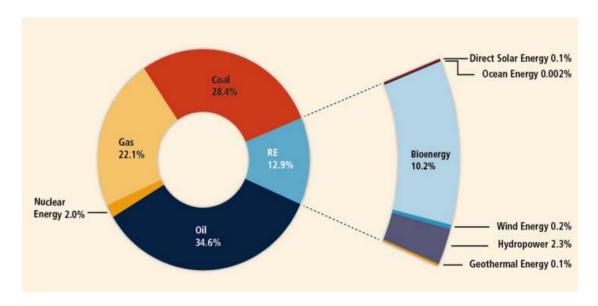


Figure 1.1. Shares of energy sources in total global primary energy supply in 2008

Most of the biomass gasifier models are thermodynamic equilibrium based models where Gibbs reactor is used to simulate different zones. This approach is based on Gibbs free energy minimization which is good at estimating final syngas composition but it cannot predict temperature profile across reactor. The multi-zonal procedure is based on rigorous kinetic models implemented on different zones of a biomass downdraft gasifier. This approach allows us to determine temperature profile across reactor and effect of gasification temperature on the syn-gas composition. A schematic of down draft gasifier is shown in Figure 1.3 [6].

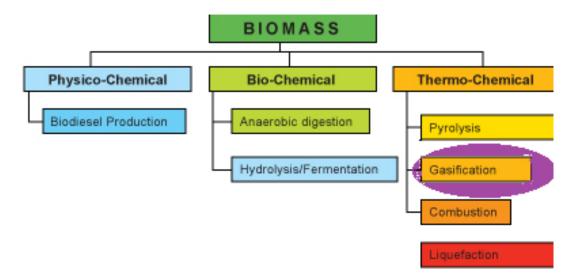


Figure 1.2. Energy pathways for biomass

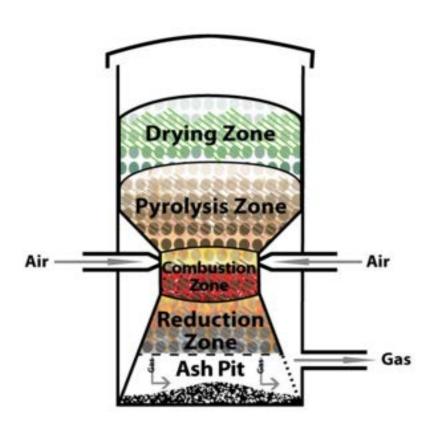


Figure 1.3. Down-Draft Gasifier

2. FEED

Examination of biomass material properties is necessary in simulation. As fuels differ greatly in their chemical, physical and morphological properties, they have different demands in methods of gasification [7]. Depending on locality, type of wood available changes. Some factors which has to be considered are ash content, moisture content, density of wood and amount of volatile inside the wood. High ash content can lead all ashes fuse together at high temperature. Usually when density of a wood is higher, it has also higher energy content for the same volume.

Biomass is defined in terms of proximate and ultimate analysis. Ultimate analysis gives the elemental composition of biomass. Proximate analysis gives the volatile matter that determines the components liberated at high temperature, fixed carbon which is the residue after the volatile is driven off, ash and moisture content. Proximate analysis is related to heating of biomass via the relative proportions of fixed carbon (FC) and volatile matter (VM). Different combinations of these mass-based result in different bulk properties such as density and heating value [8]. To study this effect, our simulation uses three different types of wood as feed materials.

2.1 TYPES OF FEED

At our Missouri S&T Energy Center Lab, we use three types of wood to run the biomass gasifier which are pellets, flakes and chips as shown in Figure 2.1. Pellet fuels (or pellets) are biofuels made from compressed organic matter or biomass. Pellets can be made from any one of five general categories of biomass: industrial waste and co-products, food waste, agricultural residues, energy crops, and virgin lumber. Wood pellets are the most common type of pellet fuel and are generally made from compacted sawdust and related

industrial wastes from the milling of lumber, manufacture of wood products and furniture, and construction.

Flakes are thin curly wood shavings used for packing or stuffing. Woodchips are made by cutting, or chipping, larger pieces of wood. They may be used as an organic mulch in gardening, landscaping, restoration ecology, bioreactors for denitrification and mushroom cultivation.

2.2 ANALYSIS OF FEED

Proximate and ultimate analyses for the above feeds were carried by Teja Boravelli in Missouri S&T Energy Center and results are shown in Tables 2.1 and 2.2. Moisture content is considered to be the main difference between these three feeds.



Figure 2.1. Different types of feed used in Missouri S&T energy center lab

Table 2.1. Ultimate Analysis of Feed

Feed	Chips	Flakes	Pellets
Carbon	47.97	47.95	48.53
Hydrogen	5.85	6.11	5.52
Nitrogen	0.25	0.05	0.05
Oxygen	44.21	45.27	44.81
Ash	1.7	0.6	0.98

Table 2.2. Proximate Analysis of Feed

Feed	Chips	Flakes	Pellets
Volatile Matter	79.88	79.47	83.01
Fixed Carbon	18.4	19.91	16
Ash	1.7	0.6	0.98
Moisture	35.19	20	7.56

3. ASPEN PROCESS MODEL

3.1 MULTIZONAL MODELING

The overall gasification process is simulated by Anand Alembath and Hassan Golpour, in four separate zones as shown in Figure 1.3. Each zone is described as follows:

3.1.1 Drying Zone. Moisture content of the feed stock is an important factor to be able to stabilize a good combustion bed while having high moisture feed and to determine if the gasifier is capable to run in a steady state condition for a long time. Also the heating value of the gas produced depends on the moisture content of the feedstock. Moisture content can be determined on a dry basis as well as on a wet basis method. In this study the dry basis method was used to calculate the moisture content as shown in equation below. The vaporization of water to steam requires a heat input of 1000 Btu/lb. of water [9]. Energy which could be useful in steam production is diverted to drying the wood fuel. So high moisture content reduces the thermal efficiency and results in low heating value of produced gas. Also, in downdraft gasifiers, high moisture contents give rise to low temperatures in the combustion zone which leads to high tar formation. Moisture content and heating value for different types of biomass are shown in Figure 3.1 below.

FUEL TYPE	MOISTURE CONTENT	HEATING VALUE
Green Wood	50%	9.5 MJ/kg
Seasoned Wood	20%	15.5 MJ/kg
Dry Sawdust	13%	16.2 MJ/kg
Wood Pellets	10%	16.8 MJ/kg
Dry Wood (Non-resinous)	0%	19.0 MJ/kg
Dry Wood (Resinous)	0%	22.5 MJ/kg
Dry Stemwood	0%	19.1 MJ/kg

Figure 3.1. Heating values for types of woody biomass sources

Moisture content = [(Wet weight - Dry weight) / Dry weight]*100

The modeling part of drying zone includes a yield reactor with a separator which removes water vapor .Free water is separated from the wet biomass. Water vapor along with dry biomass is sent to pyrolysis zone.

3.1.2 Pyrolysis Zone. Pyrolysis is where the volatile component vaporizes to a mixture of gases (de-volatilization). This process is a function of temperature and concentration of volatile and usually happens from 500 to 900 K. The volatile vapor mainly consists of hydrogen, carbon monoxide, carbon dioxide, methane, hydrocarbon gases, tar, and water vapor. As biomass has high volatile content, pyrolysis is an important step in biomass gasification. Remaining Solid char and ash are also produced in this step. Primary products characterized by compounds derived from cellulose, hemicellulose or lignin [10]. The pyrolysis reaction in aspen is modeled as a three step reaction:

Devolatilization: Biomass fuel decomposes to volatiles, char and ash. This devolatilization is a one-step reaction modeled in a yield reactor.

Primary pyrolysis: In this step, light gases are driven off along with tar from volatiles.

Volatile \longrightarrow 0.268 CO + 0.295 CO₂ + 0.094 CH₄ + 0.5H₂+ 0.255H₂0+0.004NH₃ +0.0002H₂S + 0.2 primary tar

Primary tar composition is given as $C_{6.607}H_{11.454}O_{3.482}$ [11]. Reaction rate is given by: $Rp1=4.38*10^9exp~(-1.527*10^5/RT_s)~C_{volatile}$

Secondary pyrolysis: characterized by phenols and olefins.

Primary tar \longrightarrow 0.261 secondary tar + 2.6CO + 0.441 CO₂+ 0.983 CH₄ + 2.161H₂ + 0.408C₂H₄

Secondary tar is assumed to be pure benzene [11]. Reaction rate for the secondary pyrolysis is given by: $Rp2=4.28*10^6 exp (-1.08*10^5/RTg) C_{primary tar}$

- **3.1.3 Combustion Zone.** Char reactions are considered unreacted shrinking core model which assumes char particles to be spherical; grains and solid-gas phase reaction takes place on the external surface [11]. Combustion reactions are modeled with two types of reaction:
- 1. Char oxidation reactions

$$C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

2. Hydrogen combustion reaction

$$H_2 + O_2 \longrightarrow H_2O$$

In downdraft gasifiers, generally air is introduced in the combustion zone which has a large volume of nitrogen. This dilutes the syngas and reduces the concentration of hydrogen (H₂) and carbon monoxide (CO), which reduce syngas heat value [12]. For this reason, in our simulation we have replaced air with oxygen which determines the product and temperature distribution of a gasification system.

Combustion zone is the zone which provides energy to endothermic pyrolysis and gasification reactions. Heat required for pyrolysis is between 1.6 - 2.2 kJ/g which is equal to 6 - 10% of heat of combustion of dry biomass [13]. This heat is provided by combustion of char and other volatiles. For this reason, temperature at combustion zone is higher compared to other zones. Typical temperature range for combustion zone is between 950-1150°C [14]. The lower tar concentration in downdraft reactors are due to gas passing

through a high temperature zone (the combustion zone). Since the temperature in combustion zone is high, the tar cracking reaction is specified in this zone.

3.1.4 Gasification Zone. Gasification zone is the most critical zone in a gasifier. The hot gases and carbon burnt goes through a series of reduction reactions. Temperature in gasifier zone is less compared to combustion zone and this is due to endothermic reactions. The temperature drop will depend on the extent of reactions. Ideally, as char moves downwards, char-gas reactions along with shrinking of particles leads to a decrease in char size and increase in porosity leading to more active sites and thereby increasing the conversion of char [15]. To account this mechanism, multi-phase char reaction model is written in a FORTRAN subroutine [16]. Important reduction reactions taking place in gasification zone are as follows:

1. Char Gasification Reactions

$$C + H_2O \longrightarrow CO + H_2$$

$$C + CO_2 \longrightarrow 2CO$$

$$C + 2H_2 \longrightarrow CH_4$$

2. Water Shift Reactions

$$CO + H_2O \longrightarrow CO_2 + H_2$$

3.2 ASPEN UNIT MODELS

Each unit operation in Figure 3.2 is explained in detailed in Table 3.1.

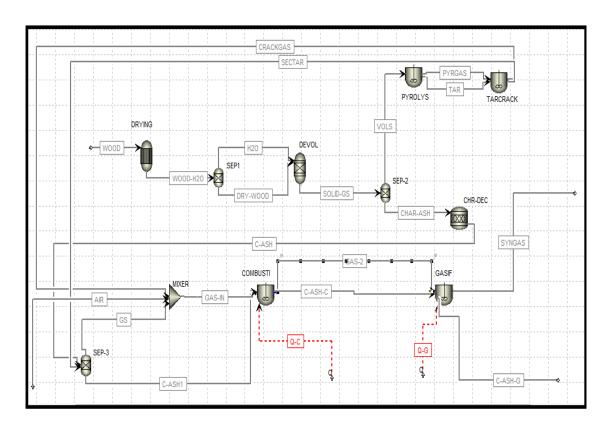


Figure 3.2. Aspen Simulated Model

Table 3.1. Aspen Unit Model

Aspen Unit Block	Function	Specification
DRYING WOOD WOOD-H20	Yield reactor removes free moisture present in biomass.	Temperature: 373K Pressure: 1atm Yield: water: 8% (for pellets) dry-wood: 92%
SEP1 WOOD-H20 DRY-WOOD	Component separator Separates water from Dry-wood.	Flash Pressure:1atm Split fraction: 1 for water and 0 for dry- biomass in stream H ₂ O.
DEVOL DEVOL DRY-WOOD SOLID-GS	Yield reactor converts dry biomass + water into volatiles, char and ash.	Temperature: 673K Pressure:1atm Yield: Volatiles: 84% Char: 15% Ash: 1%

Table 3.1. Aspen Unit Model (Cont.)

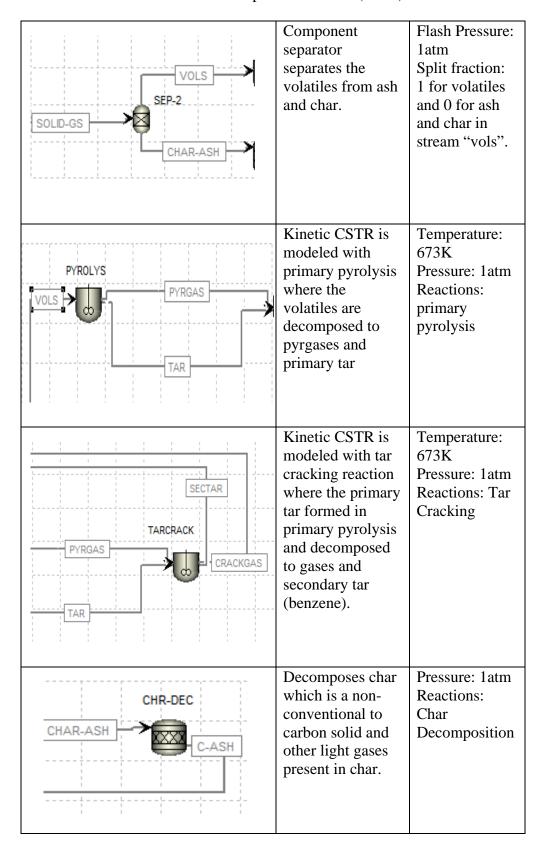


Table 3.1. Aspen Unit Model (Cont.)

SECTAR GS C-ASH SEP-3 C-ASH1	Carbon and Ash formed from devolatilization and secondary tar are separated to a gas and a solid stream.	Flash Pressure: 1atm Split fraction: 1 for light gases in GS stream and 0 for ash, C (Solid) and Secondary tar in stream "C- ASH1".
GAS-IN GAS-IN	Mixes incoming oxygen with other gas stream split from the splitter from pyrolysis and char decomposition to be used as fuel for combustion zone.	Pressure: 1atm Valid phase: vapor
GAS-IN C-ASH-C	Kinetic CSTR is modeled with a set of combustion reactions.	Pressure: 1atm Duty: Q-C Reactions: Combustion & Tar Cracking
GAS-2 GASIF SYNGAS C-ASH-C Q-G Q Q	Kinetic CSTR is modeled with a set of gasification reactions.	Pressure: 1atm Duty: Q-G Reactions: Gasification Reactions

4. RESULTS AND DISCUSSION

In this part the results are shown in three sections for three different types of feed introduced before. In each section it is shown how the best optimum case is selected. Since the quality of syn-gas is defined based on the concentration of H₂ and CO, the optimum temperature is chosen as the point where the highest production of hydrogen and carbon monoxide is achieved with priority of hydrogen. For this reason, it is first shown how the quality of produced syn-gas changes with the temperature of gasification zone. Then based on this gasification temperature, the corresponding combustion temperature and air flow are found. Finally temperatures of different zones inside the reactor are shown for the chosen optimum point.

4.1 PELLETS (8% MOISTURE)

Figure 4.1 shows the variation of mole fraction of hydrogen and CO with gasification temperature. It is observed that the optimum point is at 1199 K where there is 25% H₂ and 32% CO in produced gas.

It is obvious that the bed temperatures inside the reactor change with the change in air flow. As air flow into the reactor increases, it will increase the temperature in gasification and combustion bed as shown in Figure 4.2. Based on the optimum temperature found from Figure 4.1, the corresponding combustion temperature and oxygen flow rate are found to be 1522 K and 0.25 kg/hr respectively. The Temperature for different zones for pellets inside the reactor is shown in Figure 4.3. As mentioned before, the temperature in drying and pyrolysis zone is fixed at 373 K and 850 K respectively. This is because at those temperatures maximum amount of water is removed from the raw feed in drying zone and also maximum conversion is achieved in pyrolysis reaction.

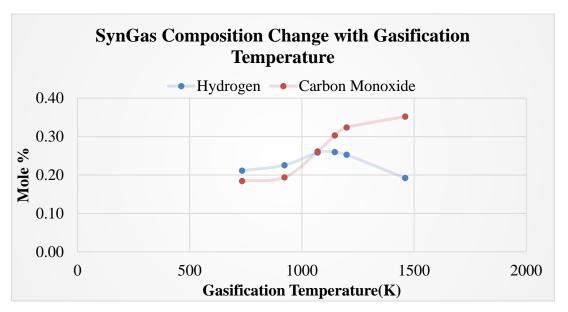


Figure 4.1. Syn-gas Composition vs Temperature

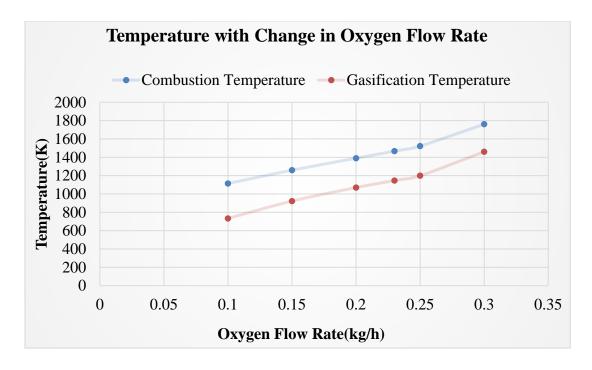


Figure 4.2. Temperature vs Oxygen flow rate

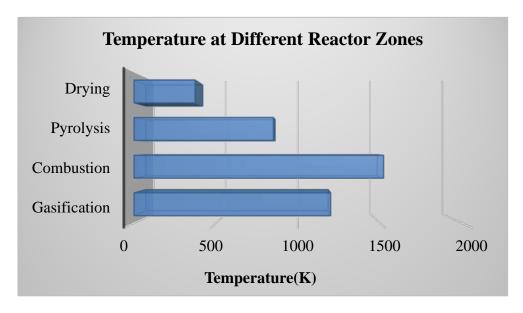


Figure 4.3. Temperature profile for pellet feed

4.2 FLAKES (20% MOISTURE)

It is observed that the optimum gasification temperature is at 1199 K where there is 23% H₂ and 27% CO in produced gas. The quality of syngas has decreased for flakes which have higher moisture content than pellets.

Optimum gasification temperature we get for flakes is 1226K. The corresponding oxygen flow rate is 0.27 kg/h and combustion temperature is 1551K. The temperature for different zones for flakes inside the reactor is shown in Figure 4.6. Flakes have slightly higher temperature at the combustion zone and gasification zone compared to pellets.

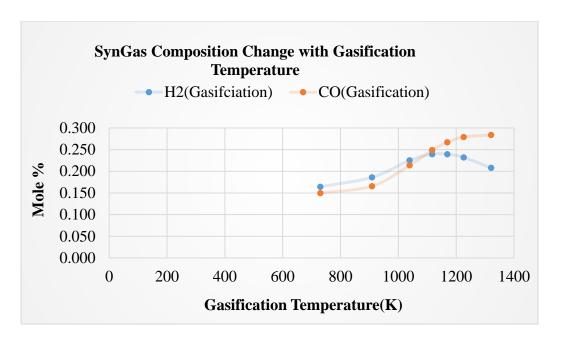


Figure 4.4. Syn-gas Composition vs Temperature for flakes

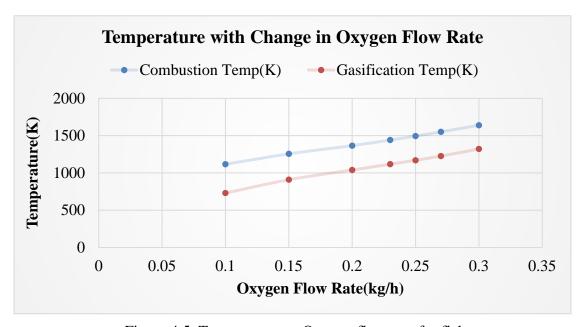


Figure 4.5. Temperature vs Oxygen flow rate for flakes

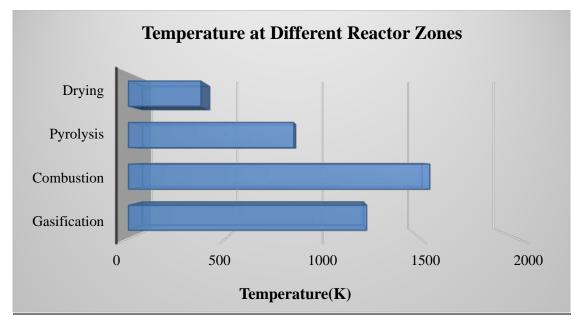


Figure 4.6. Temperature profile for flakes feed

4.3 CHIPS (35% MOISTURE)

It is observed that the optimum gasification temperature is at 1199 K where there is 20% H₂ and 15% CO in produced gas. The quality of syngas keeps decreasing with increasing moisture content. Figure 4.7 shows that hydrogen composition increases at high temperature. The mole composition increases but the flow rate of hydrogen decreases as indicated in Table 2 (Appendix A).

Optimum gasification temperature for chips is 1145K. The corresponding oxygen flow rate is 0.22 kg/h and combustion temperature is 1470K. The temperature for different zones for chips inside the reactor is shown in Figure 4.9. Chips have lower temperature in combustion and gasification zone.

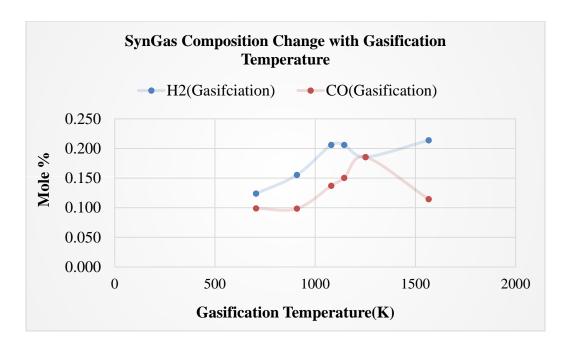


Figure 4.7. Syn-gas composition vs temperature for chips

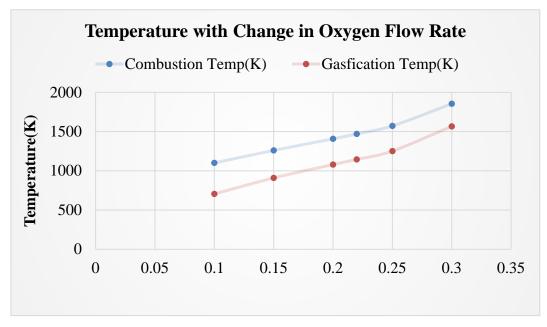


Figure 4.8. Temperature vs Oxygen flow rate for chips

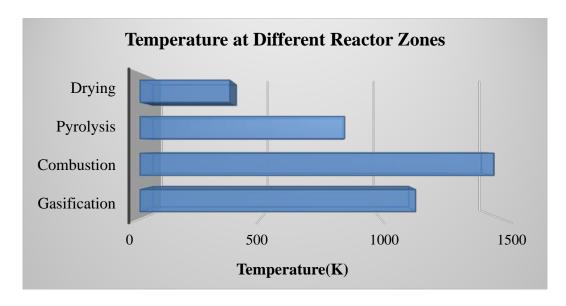
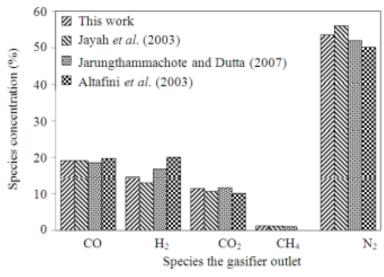


Figure 4.9. Temperature profile for chips

4.4 MODEL VALIDATION



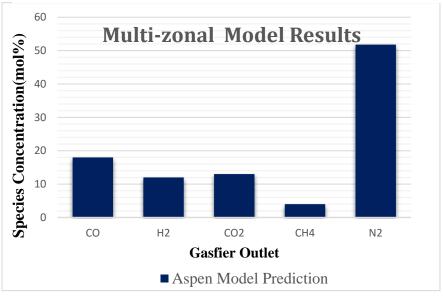


Figure 4.10. Model Validation

5. CONCLUSION

Multi-zonal modeling procedure for a downdraft biomass gasifier allows us to model different reactor zones in detail. Drying zone is modeled using a yield reactor which removes free water from biomass. Three-step devolatilization model which includes primary devolatilization, pyrolysis and tar cracking is modeled as a part of pyrolysis zone. All three reactions are modeled at same temperature. Combustion reactions are a combination of char oxidation reactions and volatile combustion reaction. Tar cracking conversion happens at higher temperature. So it is also specified at combustion zone. Gasification zone is modeled primarily with char gasification reactions along with water gas shift reaction. Multizonal modeling approach identified the critical impact of gasification temperature on syngas composition. Results show that at low temperature, the amount of CO/H₂ produced is less and at high temperatures (above 1300K) combustion happens in gasification zone leading to less quality syngas.

This model identified that oxygen used determines the products and temperatures of reaction. Oxygen consumed is plotted against gasification temperature. Syngas production is plotted against gasification temperature to accurately predict the optimum gasification temperature. Moisture content in biomass is an important factor which determines the quality of syn gas in down-draft gasifier. Effect of moisture content is studied using proximate and ultimate analysis of various feeds available at Missouri S&T Energy Center. Model predicted that pellet feed having low moisture content produced a syngas with higher CO/H₂ ratio while chips having higher moisture content produced low quality syngas which was the same case seen during the down-draft gasifier run in Energy Center lab.

However, this modeled simulated a real biomass gasification process with acceptable results, but there are some factors which could not be captured by *ASPEN* simulation such as the shape and flow behavior of the material feeding the reactor and also the shape and geometry of the reactor itself in different zones. Using *ASPEN*, we were able to identify the size of the feed particles, bulk volume and void volume inside the reactor as well as the volume and surface area of each reactor in each zone.

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APPENDIX A ASPEN SIMULATION OF OIL SHALE PYROLYSIS

Table 1. Case 1 Feed Rate = 26 tons/day

T (°C)	Light gas production (tons/day)	Spent natural gas (kg/hr)	Shale oil (tons/day)	Spent natural gas (tons/day)	Total CO ₂ (tons/day)
350	0.005397614	0.00010532	0.06047	0.379166666	0.76035
375	0.019363297	0.00013079	0.21692	0.470833333	0.88184
400	0.050912595	0.00017593	0.57036	0.633333334	1.53147
425	0.098933391	0.00024537	1.10833	0.883333332	3.31551
450	0.144052289	0.0003206	1.61379	1.154166667	3.67853
475	0.173805837	0.00038426	1.94711	1.383333332	3.9768
500	0.191476074	0.00043866	2.14507	1.579166665	4.22348
525	0.200718503	0.0004838	2.24861	1.741666666	4.42245
550	0.20575479	0.00052546	2.30503	1.891666667	4.60242
575	0.208468008	0.00056481	2.33542	2.033333334	4.77022
600	0.209966308	0.00060301	2.35221	2.170833332	4.9319
625	0.210826841	0.0006412	2.36185	2.308333334	5.0929
650	0.211340521	0.00068056	2.3676	2.450000002	5.25838
675	0.211644229	0.00071991	2.37101	2.591666665	5.42364
700	0.211828958	0.00075926	2.37308	2.733333333	5.58877
725	0.21194695	0.00079977	2.3744	2.879166668	5.75869
750	0.21202346	0.00084144	2.37526	3.029166666	5.93341
775	0.212072839	0.0008831	2.37581	3.179166667	6.10811
800	0.212106193	0.00090856	2.37618	3.270833334	6.21487
825	0.21212903	0.00092593	2.37644	3.333333334	6.28765
850	0.212144566	0.00095255	2.37661	3.429166666	10.3983
875	0.212155576	0.00096991	2.37674	3.491666665	10.4711
900	0.212105886	0.00101389	2.37618	3.650000004	10.6554
925	0.212128951	0.00105903	2.37644	3.812500008	10.8446
950	0.212173214	0.00119907	2.37693	4.316666652	11.4316
975	0.212176237	0.00124653	2.37697	4.487500008	11.6305
1000	0.212178565	0.0012963	2.37699	4.66666668	11.8391

Table 2. Case 2 $T = 600 \,^{\circ}\text{C}$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO ₂ (tons/day)
5	600	316321.002	0.445210326	0.006554043
10	600	633829.404	0.893119717	0.013111188
15	600	951636.59	1.34170827	0.01966911
20	600	1269614.64	1.79068522	0.026227482
25	550	1.46E+06	2.213004	0.032760979
30	513	1.46E+06	2.50936109	0.004093126
35	480	1.46E+06	2.65403288	0.045708433
40	455	1.46E+06	2.68112764	0.051540326
45	444	1.46E+06	2.63851848	0.057391457
60	416	1.46E+06	2.55413322	0.064212705

Table 3. Case 3 $T = 350 \,^{\circ}\text{C}$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO ₂ (tons/day)
50	350	567847.88	0.017805304	0.127426584
100	350	1151836.02	0.0356191	0.332153065
150	324.239403	1.46E+06	0.053784776	0.134792029
200	277.00078	1.46E+06	0.06158315	0.008915642
250	244.900855	1.46E+06	0.091622027	0.001047754

Table 4. Case 3 $T = 400 \, ^{\circ}C$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO ₂ (tons/day)
20	400	356544.226	0.361513563	0.025752094
40	400	752590.756	0.881736143	0.051650763
60	400	1166876.3	1.4752379	0.073777216
80	400	1593575.78	2.11861528	0.098366199
100	374.84	1.46E+06	1.11314742	0.121128936

Table 5. Case 3 $T = 450 \,^{\circ}\text{C}$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO2 (tons/day)
10	450	312059.165	0.523697584	0.012664713
20	450	652305.057	1.14390557	0.026103949
30	450	1001821.49	1.79585558	0.040234904
40	450	1356943.81	2.46699994	0.05107623
50	433.23	1.46E+06	2.55413322	0.063388944
60	416.72	1.46E+06	2.31537283	0.077190055

Table 6 - Case 3 $T = 500 \, ^{\circ}\text{C}$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO2 (tons/day)
10	500	449362.773	0.779463039	0.01334808
20	500	912734.088	1.60033669	0.025760898
30	500	1379901.21	2.43243112	0.040178714
40	458.99	1.46E+06	2.68112764	0.052189279
50	444.33	1.46E+06	2.63851848	0.056670717
60	433.23	1.46E+06	2.55413322	0.062963278

Table 7. Case 3 T = 550 °C

Feed rate		Heat Duty	Shale Oil	
(tons/day)	T (°C)	(W)	(tons/day)	CO2 (tons/day)
5	550	272586.788	0.428574492	0.006647613
10	550	548438.928	0.865574105	0.001367061
15	550	825130.721	1.30474015	0.019968887
20	550	1102304.36	1.74514943	0.026632613
25	550	1379807.65	2.18640927	0.033297463
30	513.19	1.46E+06	2.50936109	0.039797862
35	480.06	1.46E+06	2.65403288	0.004749788
40	458.99	1.46E+06	2.68112764	0.051158858
45	444.33	1.46E+06	2.63851848	0.057200293
50	433.23	1.46E+06	2.55413322	0.063180657

Table 8. Case 3 $T = 600 \,^{\circ}\text{C}$

Feed rate (tons/day)	T (°C)	Heat Duty (W)	Shale Oil (tons/day)	CO2 (tons/day)
	Ì	, ,	,	` '
5	600	316321.002	0.445210326	0.006554043
10	600	633829.404	0.893119717	0.013111188
15	600	951636.59	1.34170827	0.01966911
20	600	1269614.64	1.79068522	0.026227482
25	550	1.46E+06	2.213004	0.032760979
30	513	1.46E+06	2.50936109	0.004093126
35	480	1.46E+06	2.65403288	0.045708433
40	455	1.46E+06	2.68112764	0.051540326
45	444	1.46E+06	2.63851848	0.057391457
60	416	1.46E+06	2.55413322	0.064212705

Table 9. Case 4 T = 450 °C Feed Rate = 40 tons/day

Volume of				
reactor		Heat Duty	Shale Oil	
m3	T (°C)	(W)	(tons/day)	CO2 (tons/day)
0.005	450	862486.046	0.843076064	0.046760115
0.010	450	997773.799	1.30629675	0.047352165
0.015	450	1086393.97	1.6097292	0.047977911
0.020	450	1150101.13	1.82786037	0.048076019
0.025	450	1198652.46	1.99409848	0.048117828
0.030	450	1237176.31	2.12600284	0.048827695
0.035	450	1268663.09	2.23381251	0.049362923
0.040	450	1294990.27	2.32395589	0.048680639
0.045	450	1317403.89	2.40069937	0.048741027
0.050	450	1336767.57	2.46699994	0.048781726
0.055	450	1353701.09	2.52497976	0.048809148
0.060	450	1368662.22	2.57620616	0.049848431
0.065	450	1381997.25	2.62186483	0.049059075
0.070	450	1393973.54	2.66287126	0.04910593
0.075	455.11	1.46E+06	2.80703063	0.049267388
0.080	454.24	1.46E+06	2.82070063	0.049282417
0.085	453.42	1.46E+06	2.83347647	0.049296417
0.090	452.66	1.46E+06	2.84546293	0.04930951
0.095	451.94	1.46E+06	2.85674754	0.0493218
0.100	451.27	1.46E+06	2.86740415	0.049333373
0.105	450.63	1.46E+06	2.87749564	0.0493443
0.110	450.03	1.46E+06	2.88707597	0.049354644
0.115	449.46	1.46E+06	2.8961918	0.049364469
0.120	448.91	1.46E+06	2.90488374	0.049373808
0.125	448.40	1.46E+06	2.91318735	0.049382711
0.130	447.90	1.46E+06	2.92113396	0.049391211
0.135	447.43	1.46E+06	2.92875127	0.049399338
0.140	446.98	1.46E+06	2.93606394	0.049407126
0.145	446.54	1.46E+06	2.94309396	0.049414599
0.150	446.12	1.46E+06	2.94986109	0.049421778
0.155	445.72	1.46E+06	2.95638307	0.04942868
0.160	445.33	1.46E+06	2.96267596	0.04943533
0.165	444.96	1.46E+06	2.9687543	0.049441738
0.170	444.60	1.46E+06	2.97463131	0.049447927
0.175	444.25	1.46E+06	2.98031903	0.049453901
0.180	443.92	1.46E+06	2.98582848	0.049459683

Table 9 (Cont.)

Volume of		Heat Duty	Shale Oil	
reactor m3	T (° C)	(W)	(tons/day)	CO2 (tons/day)
0.185	443.59	1.46E+06	2.99117	0.04947
0.19	443.27	1.46E+06	2.99635	0.04947
0.195	442.97	1.46E+06	3.00138	0.04948
0.2	442.67	1.46E+06	3.00627	0.04948
0.205	442.38	1.46E+06	3.01103	0.04949
0.21	442.1	1.46E+06	3.01565	0.04949
0.215	441.83	1.46E+06	3.02016	0.0495
0.22	441.56	1.46E+06	3.02454	0.0495
0.225	441.31	1.46E+06	3.02882	0.0495
0.23	441.06	1.46E+06	3.03299	0.04951
0.235	440.81	1.46E+06	3.03706	0.04951
0.24	440.57	1.46E+06	3.04103	0.04952
0.245	440.34	1.46E+06	3.04491	0.04952
0.25	440.11	1.46E+06	3.0487	0.04952
0.255	439.89	1.46E+06	3.05241	0.04953
0.26	439.67	1.46E+06	3.05603	0.04953
0.265	439.46	1.46E+06	3.05958	0.04954
0.27	439.25	1.46E+06	3.06305	0.04954
0.275	439.05	1.46E+06	3.06645	0.04954
0.28	438.85	1.46E+06	3.06978	0.04955
0.285	438.66	1.46E+06	3.07304	0.04955
0.29	438.47	1.46E+06	3.07624	0.04955
0.295	438.28	1.46E+06	3.07937	0.04956
0.3	438.1	1.46E+06	3.08244	0.04956

APPENDIX B ASPEN SIMULATION OF BIOMASS GASIFICATION

Table 1. Simulation results for pellets

Oxygen Flow Rate (kg/hr)	Component	Mole % Combustion Zone	Mole % Gasification Zone
	CO	0.188	0.184
	H_2	0.208	0.211
	CO_2	0.194	0.197
0.1	H ₂ O	0.356	0.352
	CH ₄	0.05	0.05
	C_6H_6	0.004	0.004
	CO	0.218	0.194
	H_2	0.199	0.226
0.15	CO_2	0.186	0.21
0.15	H ₂ O	0.362	0.337
	CH ₄	0.03	0.029
	C ₆ H ₆	0.004	0.004
	CO	0.299	0.261
	H_2	0.212	0.258
0.2	CO ₂	0.16	0.198
0.2	H_2O	0.306	0.263
	CH ₄	0.019	0.016
	C ₆ H ₆	0.004	0.004
	CO	0.338	0.261
	H_2	0.21	0.258
0.23	CO_2	0.149	0.198
0.23	H_2O	0.281	0.263
	CH ₄	0.018	0.016
	C_6H_6	0.003	0.004
	CO	0.355	0.324
	H_2	0.203	0.253
0.25	CO_2	0.146	0.179
0.23	H_2O	0.274	0.226
	CH ₄	0.019	0.014
	C_6H_6	0.003	0.003
	CO	0.372	0.352
	H_2	0.158	0.192
0.3	CO_2	0.152	0.175
0.5	H ₂ O	0.285	0.25
	CH ₄	0.029	0.027
	C_6H_6	0.003	0.003

Table 2. Simulation results for flakes

Oxygen Flow Rate (kg/hr)	Component	Mole % Combustion Zone	Mole % Gasification Zone
0.1	CO	0.152	0.15
	H_2	0.162	0.164
	CO_2	0.161	0.164
0.1	H_2O	0.484	0.482
	CH ₄	0.037	0.037
	C_6H_6	0.003	0.003
	CO	0.182	0.166
	H_2	0.168	0.186
0.15	CO_2	0.164	0.18
0.15	H_2O	0.462	0.445
	CH ₄	0.021	0.02
	C_6H_6	0.003	0.003
	CO	0.247	0.214
	H_2	0.186	0.225
0.2	CO_2	0.155	0.188
0.2	H_2O	0.395	0.358
	CH ₄	0.014	0.012
	C_6H_6	0.003	0.003
	CO	0.285	0.249
	H_2	0.192	0.239
0.23	CO_2	0.148	0.186
0.25	H ₂ O	0.359	0.313
	CH ₄	0.013	0.01
	C_6H_6	0.003	0.003
	CO	0.302	0.267
	H_2	0.189	0.239
0.25	CO_2	0.146	0.184
0.23	H_2O	0.346	0.296
	CH ₄	0.014	0.011
	C_6H_6	0.003	0.003
	CO	0.312	0.267
	H_2	0.189	0.239
0.27	CO_2	0.146	0.184
0.27	H_2O	0.346	0.296
	CH ₄	0.014	0.011
	C_6H_6	0.003	0.003
	CO	0.312	0.279
	H_2	0.18	0.232
0.3	CO_2	0.148	0.185
	H_2O	0.342	0.29
	CH ₄	0.015	0.012
	C_6H_6	0.003	0.003

Table 3. Simulation results for chips

Oxygen Flow Rate (kg/hr)	Component	Mole % Combustion Zone	Mole % Gasification Zone
	CO	0.101	0.099
	H_2	0.122	0.124
	CO_2	0.141	0.143
0.1	H ₂ O	0.605	0.603
	CH ₄	0.028	0.028
	C ₆ H ₆	0.002	0.002
	CO	0.117	0.098
	H_2	0.135	0.155
0.45	CO_2	0.157	0.176
0.15	H ₂ O	0.571	0.551
	CH ₄	0.016	0.015
	C_6H_6	0.002	0.002
	CO	0.173	0.137
	H_2	0.162	0.205
0.2	CO ₂	0.161	0.198
0.2	H ₂ O	0.488	0.445
	CH ₄	0.013	0.011
	C ₆ H ₆	0.002	0.002
	CO	0.186	0.15
	H_2	0.159	0.206
0.22	CO ₂	0.163	0.202
0.22	H ₂ O	0.476	0.428
	CH ₄	0.014	0.012
	C_6H_6	0.002	0.002
	CO	0.1905	0.16
	H_2	0.1405	0.185
0.25	CO_2	0.1713	0.206
0.25	H ₂ O	0.4789	0.432
	CH ₄	0.0167	0.015
	C ₆ H ₆	0.002	0.002
	CO	0.175	0.155
	H_2	0.092	0.114
	CO_2	0.193	0.214
0.3	H ₂ O	0.515	0.492
	CH ₄	0.023	0.023
	C ₆ H ₆	0.002	0.002

SECTION

2. CONCLUSIONS

The results of leaching test illustrated the impacts of solid to liquid ratio and pH increasing on the leachability of heavy metals and their concentration in the leachate. Many necessary steps are needed to bring a new process to commercial operation such as developing a detailed process description including detailed flow diagrams with mass and energy balances for the major process variations and feeds.

The oil shale process model developed in Aspen gives an objective to find the optimum temperature and flow rate has been satisfied. It was concluded that for a 0.05 m³ volume of reactor and 1.46*E6 BTU/hr natural gas burner, the most optimum temperature is 458°C and the corresponding optimum flow rate is 40 tons/day. Another parameter which could be analysed is the reactor volume. It was concluded that volume of the reactor definitely plays an important role in process yield. Once the heat duty limit is reached, the percentage increase in shale oil production is not much significant with increase in volume.

The gasification process of various biomass feedstocks (wood chips, pellets and flakes) were studied in the designed downdraft biomass gasifier. The biomass bed and condensation unit temperatures correlated with time were discussed. Pellets having high density and high calorific values compared to chips and flakes produced a more stable and dense flame than the other two feed.

The important point that was learnt was that, the feed rate and flow of air to the reactor played an important role for a steady state process. So an optimum level of feed and air need to be sent to the reactor to retain the steady state conditions. Stability of the bed was compared as well and as a conclusion, pellets were better than picks better than flakes. It was also observed that pellets have better flame than flakes better than picks.

Multi-zonal modeling procedure for a downdraft biomass gasifier allowed us to model different reactor zones in detail. Multizonal modeling approach identified the critical impact of gasification temperature on syngas composition. Results showed that at low temperature, the amount of CO/H₂ produced is less and at high temperatures (above 1300K) combustion happens in gasification zone leading to less quality syngas.

This model identified that oxygen used determines the products and temperatures of reaction. Oxygen consumed is plotted against gasification temperature. Syngas production was plotted against gasification temperature to accurately predict the optimum gasification temperature. Moisture content in biomass was an important factor which determined the quality of syn gas in down-draft gasifier.

Model predicted that pellet feed having low moisture content produced a syngas with higher CO/H₂ ratio while feed chips having higher moisture content produced low quality syngas which was the same case seen during the down-draft gasifier run in Energy Center lab.

VITA

Hassan Golpour was born on March 21, 1989. He completed his B.S. degree in Petroleum Engineering at Petroleum University of Science and Technology in August of 2010. He came to United States in June 2011 to pursue his graduate education in master level in Petroleum Engineering but after the summer semester he found Dr. Joseph D. Smith who joined the department of Chemical Engineering as a new faculty at the same summer. After a few meetings he decided to change his major and was accepted as a PhD student in Chemical Engineering and joined Dr. Joseph Smith's research group in the fall of 2011.

He was also a graduate research assistant, graduate teaching assistant, and course instructor during his time as a graduate student in the Chemical and Biochemical Engineering Department while pursuing his Ph.D. Hassan Golpour graduated with his Ph.D. in Chemical Engineering in May 2016.