

# Bio-oil production and catalytic upgrading

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## ABSTRACT

In the last few years, biomass based fuels are emerged as a sustainable source of liquid fuel to replace the petrochemicals. Our current design incorporates production of bio-oil from waste forestry residues to produce drop-in replacement to non-renewable petroleum based diesel no.2 fuel. We have developed two 2<sup>nd</sup> generation pyrolysis reactors (fast pyrolysis, 1kg/hr and Auger pyrolysis, 7kg/hr). These reactors can produce up to 65-70% biooil yield and can do in situ bio-oil upgrading to diesel fuel using solid catalysts. Several catalysts were prepared for this purposes, screened and optimized to get high yield of diesel fuel. The process is scaled up using 2kg scale catalyst.

**Keywords:** lignocellulosic feedstock, pyrolysis, catalyst, upgrading

## 1 INTRODUCTION

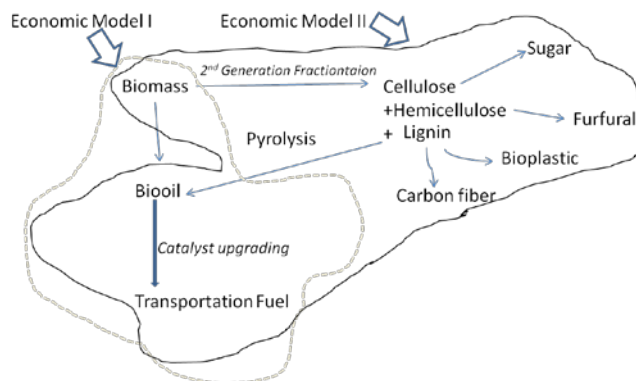
With the worldwide availability of lignocellulosic biomass of 220 billion oven-dry tons per year there has been a great deal of interest in utilizing lignocellulosic materials for the production of liquid transportable fuel or valuable products [1,2]. Currently several permits have been issued to burn woodchips to fuel old fashion power plants to generate electricity. While this process is at least a carbon neutral power generation, but it may not be the best way to use our natural resources. Conversion of the wastes from forestry and agricultural activities to bio-oil and refine the bio-oil to a liquid fuel or other high value chemical (that otherwise, must be produced from fossil fuels is becoming increasingly attractive solution. At the present, Bio-oil produced by pyrolysis has quality well below fossil fuel (about 50%). As scientists and industries are developing technologies that can upgrade low quality bio-oil to high quality carbohydrate chains, this process is becoming more and more attractive. Thermochemical conversion of biomass is one of the methods to produce usable energy from lignocellulosic biomass [3]. In the past, application of bubbling bed fast pyrolysis to produce bio-oil from woodchips and agri-wastes has been reported by many companies and universities [4,5].

Pyrolysis oil consists of a complex mixture of aliphatic and aromatic oxygenates (e.g., acids, aldehydes, ketones) and particulates (solids). It is very viscous, acidic (pH<3) and unstable liquid with relatively low energy

density (16-19 MJ/kg) compared to conventional fossil oil (42-45 MJ/kg). Bio-oil cannot be used as a transportation fuel without upgrading to improve its physical and chemical properties [6]. The progress in this field is not fast enough to achieve our nation's target to be energy independent. If the biooil can be produced in high yield and more economical way then it be directly used as a fuel blen and/or as upgraded liquid transportable fuel. The objective of this study is to evaluate the economic viability and commercialization potential of the fast pyrolysis processes and auger pyrolysis and biooil upgrading.

## 2. LARGE SCALE PYROLYSIS

We approach two different ways to make biooil: 1) by direct biomass pyrolysis and 2) fractionation followed by pyrolysis (Figure 1). Experiments will be conducted to produce biooil with each of the three designated feedstocks (woody biomass, corn stover and grass).



**Figure 1:** Two different approaches to make biooil are evaluated using fast and auger pyrolysis.

## 3. EXPERIMENTAL

### Pilot Scale Lignin Production:

AST's integrated bio-refinery process summarizing butanol organosolv pretreatment, separation and purification stages as well as solvents (butanol and water) recovery units is shown in Figure 2. Lignocellulosic raw material will be treated in aqueous butanol, in a pilot scale 20 kg batch reactor with temperature and pressure control. Experimental

conditions will be used are: butanol–water 50/50 m/m; temperature: 160-180 °C; reaction time: 30 min; liquid/solid ratio: 5:1. After fractionation, the liquid are collected to a separate container where the lignin-liquor and hemicelluloses are separated. The cellulose (solid) are centrifuged to collect the adsorbed solvents in the fiber; washed with water and process for enzymatic hydrolysis. The average cellulose yield is generally 40-45 wt%. The butanol (and other chemicals like furfural and esters, Figure 3) from the liquor are distilled off to produce high quality lignin. In this process 90-95% lignin is recovered from the biomass. This lignin is of high purity with melting properties around 178 C and soluble in wide range of organic solvents. These properties make this lignin a strong candidate to replace petrochemical based feedstocks to produce plastics and carbon fiber. The aqueous solvent (water, acid and partial soluble butanol) is recycled in the next recycle. In the fractionation process over 60% of the total C5 sugars are converted to furfural which is collected in the butanol after distillation from the liquor. The organic acids from the woody biomass feedstock are partially captured in the form of esters and collected with butanol after a simple distillation process.



**Figure 2:** AST's fraction unit. This is capable of fractionating 20 kg dry biomass to produce around 4 kg of high quality lignin.

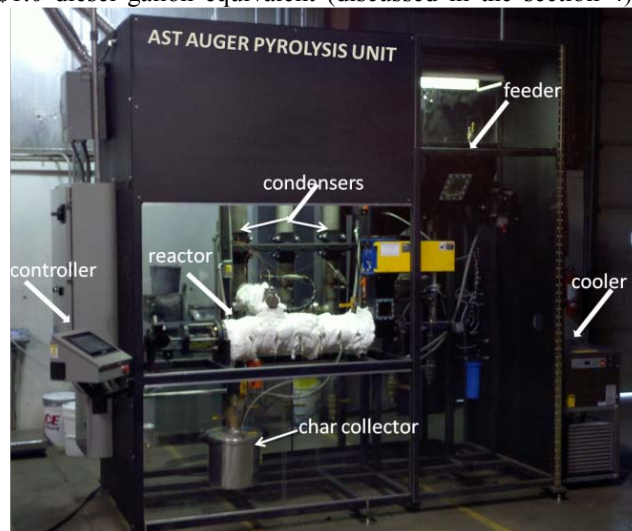
### Fast Pyrolysis:

AST has designed a fast pyrolysis reactor that can pyrolyze woody biomass at 1kg/h. The bubbling bed is also designed such a way that it allows for the online incorporation of catalysts in the pyrolysis process for hydrodeoxygenation process and/or replacing sand with catalysts for cracking reactions. The system is optimized using saw dust as feedstock. Various parameters such as particle sizes, feed rate, bubbling rate/volume, reactor temperature are optimized to get the maximum bio-oil yield. Under the best

conditions a maximum of 55 % bio-oil yield was obtained. Pyrolysis of saw dust is easier to perform than the lignin. This unit is also successfully evaluated for the pyrolysis of rubber and coal.

### Auger Pyrolysis:

AST has successfully manufactured an auger pyrolysis unit with 7kg/hr feedstock input. This unit is optimized for woody biomass with a yield of biooil is around 70%. Pyrolysis experiments are carried out in Auger pyrolysis unit located in AST (Figure 3). Its unique design drops biomass from a hopper, at an adjustable rate, to a heated reactor. The reactor temperature is controlled very precisely by a series of heaters and a state-of-the-art control system, which heats the biomass to very high temperatures (typically 400-500 °C), and using a special internal auger, moves the converted biomass solid product (char) towards a char collection bin. The vapors released from the pyrolysis process inside the reactor are directed downstream towards a series of four condensers that use a special cooling system to rapidly quench them and direct the oil to collection containers. Figure 4A shows a picture of the bio-oil produced at AST. Figure 4B shows the GC profile of the produced bio-oil. This process will be extended to other kind of readily available biomass feedstocks (grass and corn stover). The process is designed to get a bio-oil yield of 70%, which makes the produced bio-oil competitive with petroleum fuels. At this yield, the cost of bio-oil is \$0.75 to \$1.0 diesel gallon equivalent (discussed in the section 4).

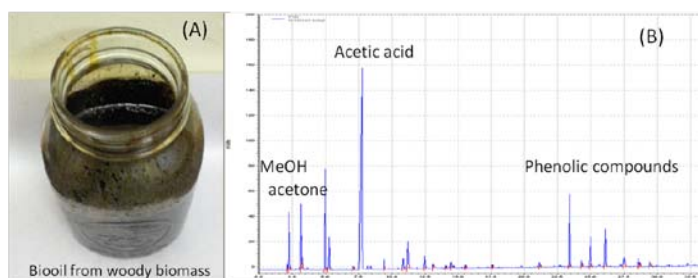


**Figure 3:** AST's Auger pyrolysis unit. This is capable of converting 7 kilograms of biomass into bio-oil every hour.

### Bio-oil upgrading:



**Small scale upgrading using phenol as the model compound:**

Hydrodeoxygenation reactions of phenol, which was employed as one of the model reactions in bio-oil upgrading, were done under different conditions. Water was used as a solvent for this reaction. The reaction is optimized by changing the reaction pressure, catalyst amount, various catalysts, reaction temperature and reaction time. The samples were collected after the reactions and analyzed by GC and the results are summarized in Table 1.



**Figure 4:** (A) biooil produced at AST using waste hardwood and (B) the GC profile of the biooil showing the typical composition of a biooil.

**Table 1:** Phenol conversion and product distribution<sup>1</sup>

Catalyst	T(°C)	P (psi)	Conv. (%)	Selectivity (%)	
					
0.5%Pt/HZSM5	140	700	76.5		100
0.5%Pt/HZSM5	140	300	68		100
0.5%Pt/HZSM5	170	300	94.8		100
1%Pt/HZSM5 <sup>2</sup>	200	300	96.2	13.2	86.8
1%Pt/HZSM5 <sup>2</sup>	140	300	85	85.6	14.4
0.5%Pt/HZSM5 <sup>3</sup>	140	300	99.2	0.2	99.8
0.5%Pt/HZSM5 <sup>4</sup>	170	300	13.3	15.8	84.2
0.5%Pt/HZSM5 <sup>2</sup>	200	300	100		100
0.5%Pt/HZSM5	200	200	91.3		100
0.5%Pt/HZSM5 <sup>5</sup>	200	300	98		100

<sup>1</sup>2g of phenol, 1g (unless otherwise noted) of catalyst, 1h

<sup>2</sup>0.5g catalyst

<sup>3</sup>0.5h

<sup>4</sup>calined in air and reduced in the reactor at 200°C and under 300psi for 2h

<sup>5</sup>The catalyst was from the previous run

### Small scale Biooil upgrading:

Under similar conditions as discussed for the deoxygenation of phenol biooil was upgraded using various acid catalyst in a 200 ml batch reactor. Mesoporous carbon, microporous zeolites, mesoporous solid acids and Amberlist catalysts were used. Effect of various metals such as Pt, Pd and Ru was investigated on these solid acid supports. Rapid screening process was used to find the suitable catalyst and reaction conditions. 100 ml biooil was used for these experiments. Activated carbon based catalysts was found to be the best catalysts for this kind of biooil upgrading. After the reaction around 20-25% upgraded oil were obtained. In this process some of the

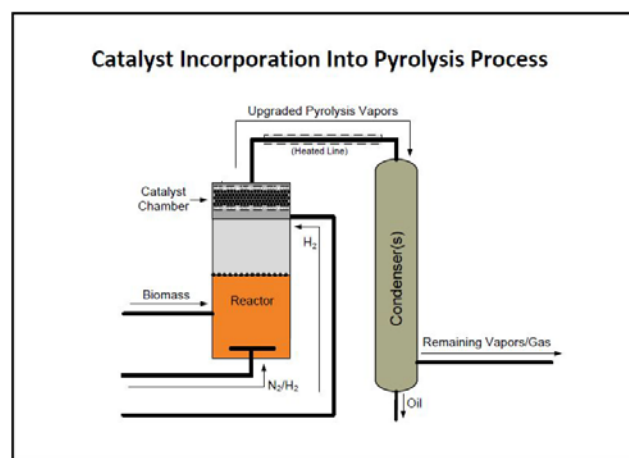
high molecular weight lignin fractions were also converted to char. After biooil upgrading over activated carbon catalyst at 300-400°C under H<sub>2</sub> contains 14% of oxygen, while the oxygen content in the original bio-oil is ~39% (Table 2). There is only about 10-15% of char produced. Other solid acid supports (mesoporous and zeolites) produced more char compared to the activated carbon catalysts. Similar observation was also observed by Kuramoto et al using mesoporous strong acid catalysts [7].

**Table 2:** water and elemental analysis of biooil before and after upgrading using solid acid catalysts.

	H <sub>2</sub> O	C	H	O
Bio-oil	38%	53.3%	7.4%	39.2%
upgraded	--	77.0%	8.7%	14.3%

### Online upgrading in the fast pyrolysis reactor:

AST has designed a second generation pyrolysis system that allows for the incorporation of catalysts in the pyrolysis process (Figure 5). A few of the various approaches accommodated for in this system include testing the performance of catalysts at the exit of the reactor for the upgrading of the pyrolysis vapor, replacing the sand in the fluidized bed with a catalyst that can both promote the heat transfer to the biomass and catalyze the pyrolysis, experimenting with the condensation of pyrolysis vapor at a variety of temperatures, and using different biomass materials such as lignin/solvent mixtures. This 2<sup>nd</sup> generation reactor is evaluated for the in situ upgrading of biooil vapours to gasoline kind fuel (Figure 6).



**Figure 5:** Schematic of the in situ bio-oil vapor upgrade during a fast pyrolysis process.



**Figure 6:** Upgraded bio-oil obtained from *in situ* hydrodeoxygenation of bio-oil during fast pyrolysis. 44% yield was obtained. The experiment was carried out using 2kg of catalyst and saw dust as the feedstock.

#### 4. ECONOMY

Economic evaluation was done based on the AST's laboratory based Auger pyrolysis (7 kg/hr) unit to produce high yield (~70%) bio-oil. Based on the presented performance, a strategically located 100 dry T/day plant, while it pays for hauling in the biomass and hauling out the bio-oil, can make money and produce 5.09 mGal of bio-oil/yr (at 70% yield, which is achievable based on the preliminary runs). For this analysis, we have assumed the bio-oil heat content is 17.9 MJ/kg (20 MJ/kg HHV for wood) and density is 4.55 kg/gal. The bio-oil heat content is almost equivalent to 50% of the #2 heating oil. We also have assumed our process can produce 70% bio-oil, 20% char, and 10% gas. Using these assumptions, a 100 T/D stationary unit can produce 4.2 million gal bio-oil per year. Our projected price to produce bio-oil is at a price of \$0.75-\$1.0 (\$1.5 to \$2.0 diesel gallon equivalent based on 50% energy content in the bio-oil). This is in line with other economic evaluations [8].

#### 5. CONCLUSIONS

Pyrolysis of woody biomass using fast and Auger pyrolysis units are demonstrated in pilot scales. Pyrolysis of whole biomass is easier to perform than fraction of woody biomass and followed by pyrolysis of lignin fraction. The later process might be more economical if the lignin can be utilized for the production of carbon fiber and bio-plastic. However the former process can produce liquid transportable fuels in a single step using a 2<sup>nd</sup> generation pyrolysis technology. These processes show enormous potential to compete with petrochemical industry and a sustainable bio-fuel economy.

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