

Process design and techno-economic evaluation of the organosolv-derived lignin pyrolysis towards platforms chemicals and biofuels

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Abstract

The process description and techno-economic analysis of lignin fast pyrolysis (thermal and catalytic) towards the production of platform chemicals (alkoxy/alkyl-phenolics and BTX aromatics) and biofuels is presented in this study. The scaled-up process is designed so as to operate in a continuous mode and consists of a) lignin feed section, b) pyrolysis under inert atmosphere, c) separation of the products into gases and condensables, d) circulation of solids (regeneration of inert material and catalyst) and e) heat recovery. The necessary data for the process scale-up (output yields, unit efficiencies, operating conditions, etc.) were derived from in-house experiments performed at Luleå University of Technology (upstream lignin derivation from lignocellulosic biomass pretreatment) and CPERI/CERTH (lignin fast pyrolysis in a fixed-bed reactor). Based on the comparison of both non-catalytic and catalytic pyrolysis for a lignin throughput of 100 tn/hr, it was identified that the quality and the amount of the bio-oil is the main parameter that can drive-up process economics, as long as the lignin price remains at a moderate value of <100 €/tn.

Introduction

Lignocellulosic biomass (such as wood, grass and agricultural waste) has the potential to provide heat, power and an extended list of high-added value chemicals through bio- or thermo-chemical processing [1]. As compared to biochemical conversion, thermochemical processes are considered to be more mature and economically feasible. Such technologies include gasification, pyrolysis and combustion and have the inherent ability to process all three constituents of lignocellulosic biomass (cellulose, hemicellulose, lignin). Among all constituents, lignin is still under-utilized towards its valorization to high-added value chemicals and fuels, as it is mainly burnt for heat/power recovery [2]. Nevertheless, its aromatic-phenolic nature makes lignin a potentially valuable source for the chemical industry.

Organosolv pretreatment/fractionation is considered one of the most promising methods for biomass delignification and can lead to the production of relatively clean streams of cellulose, hemicellulose, and lignin [3]. In this process, a mixture of organic solvents, water, catalyst and moderate operating conditions can be employed. The acquired lignin has a low ash content, is sulfur-free, and retains the majority of β -ether bonds, rendering it a suitable feedstock for the production of chemicals [4].

Regarding lignin valorisation, fast pyrolysis is a process that can produce bio-oil rich in valuable chemicals under oxygen-free conditions. Simultaneously, the produced gas and solid streams can be re-utilized in the process and minimize thermal/operating requirements in a scaled-up unit. Recent literature studies have identified that kraft-derived lignin pyrolysis can lead to improved economics when transport fuels are considered [5], whereas minimum bio-oil selling prices were identified in a similar biomass pyrolysis plant [6]. To the best of the authors' knowledge, the process analysis and techno-economics of an organosolv-derived lignin pyrolysis plant is under-investigated in literature and needs to be studied further. Hence, aim of this study is to provide a preliminary basis for identifying the economic capabilities of thermal and catalytic lignin pyrolysis, by exploiting experimental data from lab-scale units.

Process Description and Methodology

Organosolv (pre)treatment of biomass and lignin pyrolysis in lab-scale units

The necessary data (feedstock properties, operating conditions, product yields and unit efficiencies) for the validation of the scaled-up process were derived through two stages of experiments: i) lignocellulosic biomass (pre)treatment to derive pure lignin and ii) fast pyrolysis in a fixed-bed reactor using inert sand (non-catalytic) and ZSM-5 zeolite (catalytic).

i) A typical hardwood (birch) was treated at 200°C for 15 min with 60% v/v ethanol and 1% w/w_{biomass} of H₂SO₄ in a pilot scale hybrid organosolv/steam explosion reactor at Luleå University of Technology. Initially, a traditional organosolv cooking took place, followed by a rapid decompression at the end of the organosolv cooking procedure. The pretreated liquor was collected and the respective solids were separated by vacuum filtration. Next, the liquid product was collected and ethanol was removed in a rotary evaporator in order to reduce lignin solubility and facilitate its recovery. After ethanol removal, the liquor was centrifuged for 15 min and lignin was recovered as a wet paste, air-dried and further stored. Lignin was characterized and more information on the applied methodology can be found in [4].

ii) The fast pyrolysis experiments were conducted in a bench-scale fixed-bed reactor unit in CPERI/CERTH by using inert silica sand (non-catalytic) or ZSM-5 zeolite (in-situ catalytic upgrading of bio-oil vapors). The inert or Catalyst/biomass ratio was 1, temperature was set at 500 °C and recovery of products was achieved through rapid cooling. Liquid products were separated in aqueous and organic phases and analyzed through respective techniques (e.g GC-MS). Gas products were analyzed in a gas chromatograph (CO, CO₂, H₂ and C₁₋₄) whereas char and coke (solids) were determined by C/H elemental analysis and, sample weighting [7].

Process Development and Simulation

Figure 1 presents the lignin fast pyrolysis process for a throughput of 100tn/hr as simulated in Aspen Plus. The reactor configuration follows a circulating fluidized bed mode similar to a fluid catalytic cracking units [8]. Initially, lignin is fed at mild preheating to the fast pyrolysis unit. Pyrolysis takes place in a fluidized bed reactor either in non-catalytic or catalytic mode at 500°C. The exit of the reactor is separated into gaseous, solid and liquid products. Gas products can be recycled back to the pyrolysis unit in order to facilitate fluidization properties along with fresh N₂ (in order to maintain fluidization velocity above its minimum point) or used for heat recovery. Simultaneously, solid products in the form of char/coke are driven to the second reactor unit (combustor) where regeneration takes place under air combustion at 650°C. Both reactors are heat balanced, since the hot inert sand or catalyst is used to heat-up the lignin feed and maintain pyrolysis temperature (through manipulation of solid/lignin mass ratio). The heat recovery from flue gases can be utilized towards medium pressure steam generation and possible power production in turbines [8]. The received bio-oil product is gravimetrically separated into an aqueous and organic phase. The organic phase is the main product of lignin pyrolysis and comprises rich-organic chemicals.

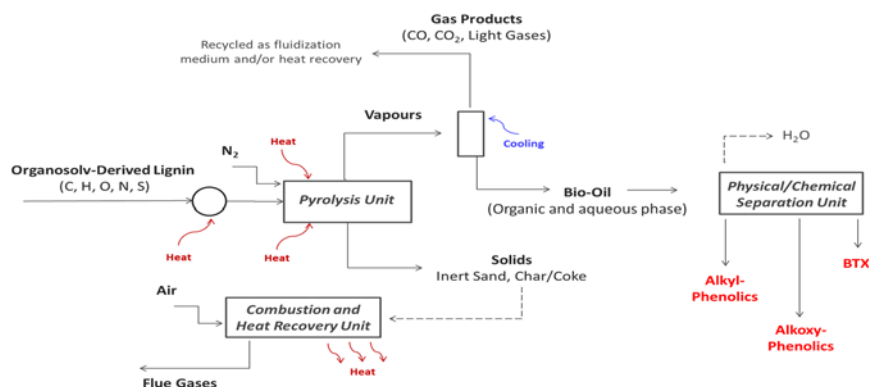


Figure 1. Schematic representation of the lignin fast pyrolysis process

As shown in Table 1, the catalytic process leads to a significantly lower liquid organic product due to the higher extent of the deoxygenation and cracking reactions. Moreover, the composition of the organics is significantly different in the two cases. Higher aromatics and phenolics are present in the catalytically upgraded organic phase, whereas higher oxy-phenolics are present in the non-catalytic organics (not shown in this study explicitly). Furthermore, the catalytic process leads to higher solid production (due to coke formation) and to higher heat recovery (through medium pressure steam generation) during regeneration. Simultaneously, 13.3% more air is required for the solid regeneration at the combustion unit, whereas cooling requirements are nearly similar in both cases.

Table 1. Process simulation results for mass & energy balances (for 100tn/hr of lignin feed)

| | Non-Catalytic | Catalytic |
|--|---------------|-----------|
| Organics (tn/hr) | 26.15 | 11.64 |
| H ₂ O (tn/hr) | 12.52 | 18.64 |
| Gases (tn/hr) | 16.16 | 21.25 |
| Solid (tn/hr) | 45.16 | 48.6 |
| Air for Combustion (tn/hr) | 301.49 | 340.45 |
| Cooling Water (tn/hr) | 1434 | 1520 |
| Steam Production (tn/hr) | 85 | 95 |
| Biogenic CO ₂ emissions (tn/hr) | 85.26 | 100.6 |

Process Design and Techno-economic Analysis

In Table 2, the preliminary economic analysis for the two processes is presented. In both cases the objective was to identify the minimum product (organics) sale price in order to have a Net Present Value equal to zero at the end of the 20 yrs lifetime operation period. Overall, the major equipment cost is similar in the two cases, since both non-catalytic and catalytic process take place in the same plant facilities. The utilities cost is higher in the catalytic process due to the need to purchase the ZSM-5 catalyst (replaced every 2-3 yrs), which also increases the total annual production cost by 14% as compared to the non-catalytic process. Therefore, the total product cost has to be higher in the catalytic process (also due to the lower bio-oil yield). This is reasonable, since the quality of the catalytic bio-oil is better due to the lower oxygen content and the high percentage of BTX aromatics and phenols. In all calculations, lignin is assumed to be purchased at a value < 100 €/tn with the produced electricity for steam generation and exploitation being sold at a fixed price of 0.17 euro/kWh.

Table 2. Preliminary economic analysis

| | Non-Catalytic | Catalytic |
|--|---------------|-----------|
| Major Equipment Cost, Meuro | 15.3 | 16.4 |
| Total Fixed Capital Investment, Meuro | 92.5 | 96.6 |
| Total Annual Production Cost, Meuro | 92.15 | 105.18 |
| Total Utilities Cost, Meuro | 71.7 | 83.6 |
| Total Product Cost, Meuro | 115.3 | 131.8 |
| Organics: Minimum Sale Price (euro/tn) | 430 | 1100 |

Conclusions

A scaled-up process analysis of a lignin pyrolysis plant towards the production of platform chemicals was assessed in this study. As was identified, the catalytic pyrolysis oil is rich in BTX aromatics and alkoxy-phenols and can lead to improved economics even though the product yield is <15 %w.t, as long as, a high sale price is established. The above results, although in preliminary stage (an optimistic scenario for lignin price was applied in this study), provide significant insights regarding issues such as product separation, energy minimization and by-product utilization in order to further improve the process economics.

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