Energy research Centre of the Netherlands

System evaluation lignin pyrolysis biorefinery

Co-operation IEA-Tasks 42 (Biorefining) & 34 (Pyrolysis)

Lille, March 3-4, Paul de Wild (ECN)

INCENTIVE

Lignin is world's 2nd biopolymer and a valuable resource for a variety of products. The pulp- and paper industry produces a huge stream of lignin containing waste (black liquor). Only a small part of the overall production is valorised to chemicals. The rest is burned for heat.

It is expected that the growth of 2nd generation production of transportation fuels like bio-ethanol will lead to an increase of the lignin containing waste stream from the biorefinery. To date, the main practised option for this stream is its use as a fuel.

Pyrolysis is an interesting option to convert the lignin into a bio-oil that is rich in valuable phenolic compounds. Possible applications include the substitution of petrochemical phenol in e.g. PF-resins and the extraction of high-value specialised phenols like guaiacols and syringols. In addition, the lignin char might be a valuable product as well, e.g. as soil-improver.

Fates of lignin

The big issue with lignin are :
-there is one cellulose, some hemicellulose and a world of lignin
-lignin are derived from processes driven by polysaccharides
-remaining lignin is not alone : what about purity and extraction?
-biorefinery are mostly aqueous processes, not compatible with lignin

To summarize, lignin is the last stream to be valorized.

Last, but not least, lignin could be also :

- an interesting guinea-pig for chemist
- a biocombustible for heat and power generation in biorefinery
- a load for feed / concrete / boards,....
- but probably the most promising building block for aromatic chemistry

Presented by F. Martel of ARD on the LIG2G seminar in Reims, France; 2007

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BACKGROUND INFORMATION

AIChE

Lignin Valorisation for Chemicals and (Transportation) Fuels via (Catalytic) Pyrolysis and Hydrodeoxygenation

Paul de Wild (ECN),[a] Ron Van der Laan, (ECN),[a] Arjan Kloekhorst (RUG),[b] and Erik Heeres (RUG)[b]
[a] Energy Research Centre of the Netherlands (ECN), Westerduinweg 3, 1755 LE Petten, The Netherlands; dewild@ecn.nl (for correspondence)
[b] University of Groningen (RUG), Nijenborgh 4, 9747 AG Groningen, The Netherlands

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New technology is needed to exploit the potential of lignin as a renewable feedstock for fuels, chemicals and performance products. Fast fluidized bed pyrolysis of different lignins at 400°C yields up to 21 wt% (d.b.) of a phenolic fraction containing 10 wt% (d.b.) of several phenols. Subsequent catalytic hydrotreating of this phenolic fraction with 100 bar of hydrogen in dodecane at 350°C yields mainly cycloalkanes, cyclohexanols and alkanes. For the production of monomeric phenols, it appears that the used ruthenium on carbon is a too active catalyst. However, cyclohexanols may be interesting products, e.g., for use as oxygenates in engine fuel. © 2009 American Institute of Chemical Engineers Environ Prog, 28: 461–469, 2009

Keywords: Lignin, Chemicals, Phenols, Cyclohexanols, Pyrolysis, Hydrotreating, Catalysis

INTRODUCTION

At present, the use of lignin is growing because of an increasing interest in renewable raw materials. Large amounts of lignin and lignin-containing residues originate from the pulp and paper industry. The expected growth of the production capacity of second-generation bio-fuels from ligno-cellulosic biomass will lead to still another source of lignin and lignin-containing residues. Nowadays, only a part of the lignin is used, despite its large potential as a significant petrochemical substitution option for fuel, performance products (polymers) and individual low-molecular-weight chemicals. Economic and technological considerations still preclude a large-scale mass production of low-molecular-weight chemicals from lignin in competition with petrochemicals. This is inherent to the specific nature of the complex and stable lignin polymer, which makes it difficult to convert it into valuable monomeric chemicals. Despite its recalcitrant nature, lignin can be broken down to monomeric or low-molecular-weight compounds by a variety of routes, such as alkaline oxidation or hydrolysis, alkali fusion, alkaline demethylation, hydrogenolysis and pyrolysis [1]. Pyrolysis is a relatively simple thermochemical route to break down lignin into low-molecular-weight compounds in the absence of oxygen (air). However, because of the physicochemical characteristics of lignin as a thermoplastic, thermally stable and often powder-like material, and because of the non-specific nature of the pyrolysis process itself, industrial lignin pyrolysis processes are rare, although in the former USSR, hydrolysis lignins from wood saccharification are considered to be valuable material for the production of phenolic compounds and activated lignin carbon. Yields of monophenols up to 10% of the lignin were obtained by pyrolysis of hydrolysis lignin in anthracene oil under reduced pressure and temperatures of 440 to 460°C [2, 3]. In literature on the gaseous phase pyrolysis of lignin for the production of chemicals, yields of

IEA Bioenergy Tasks 34 & 42 co-operation on a lignin pyrolysis bio-refinery

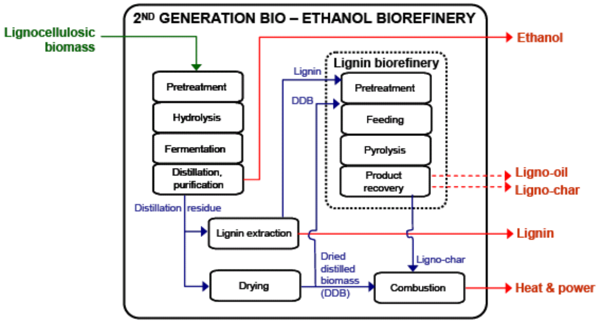
Introduction

The major objective of Task 42 - Biorefineries is to assess the worldwide position and potential of the biorefinery concept. A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, materials and/or chemicals from biomass. By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. An important activity of Task 34 - Pyrolysis is to focus on resolution of technical issues to aid commercial implementation of fast pyrolysis, e.g. within the framework of a biorefinery. As a co-operation between Task 34 and 42, Paul de Wild (ECN, NL) will conduct a case study on lignin valorization by pyrolysis to facilitate pyrolysis-based biorefineries. Paul will join the Dutch Task 42 team for the 2010-2012 period.

Background

At present, utilization of lignin is growing due to an increasing interest in renewable raw materials. Large amounts of lignin and lignin containing residues originate from the pulp- and paper industry. Within the biorefinery concept, the expected growth of the production capacity of second generation biofuels like bio-ethanol from lignocellulosic biomass will lead to another source of lignin and lignin containing residues. Despite its large potential as a significant and valuable petrochemical substitution option for fuel, performance products (polymers) and individual low molecular weight chemicals, the main practised option to date is the use as a low-cost solid fuel for generating heat. Despite its recalcitrant nature, lignin can be broken down to monomeric or low-molecular weight compounds by a variety of routes, such as alkaline oxidation or hydrolysis, alkali fusion, alkaline demethylation, hydrogenolysis, pyrolysis etc. Compared to

Figure 1 Conceptual pyrolysis based biorefinery



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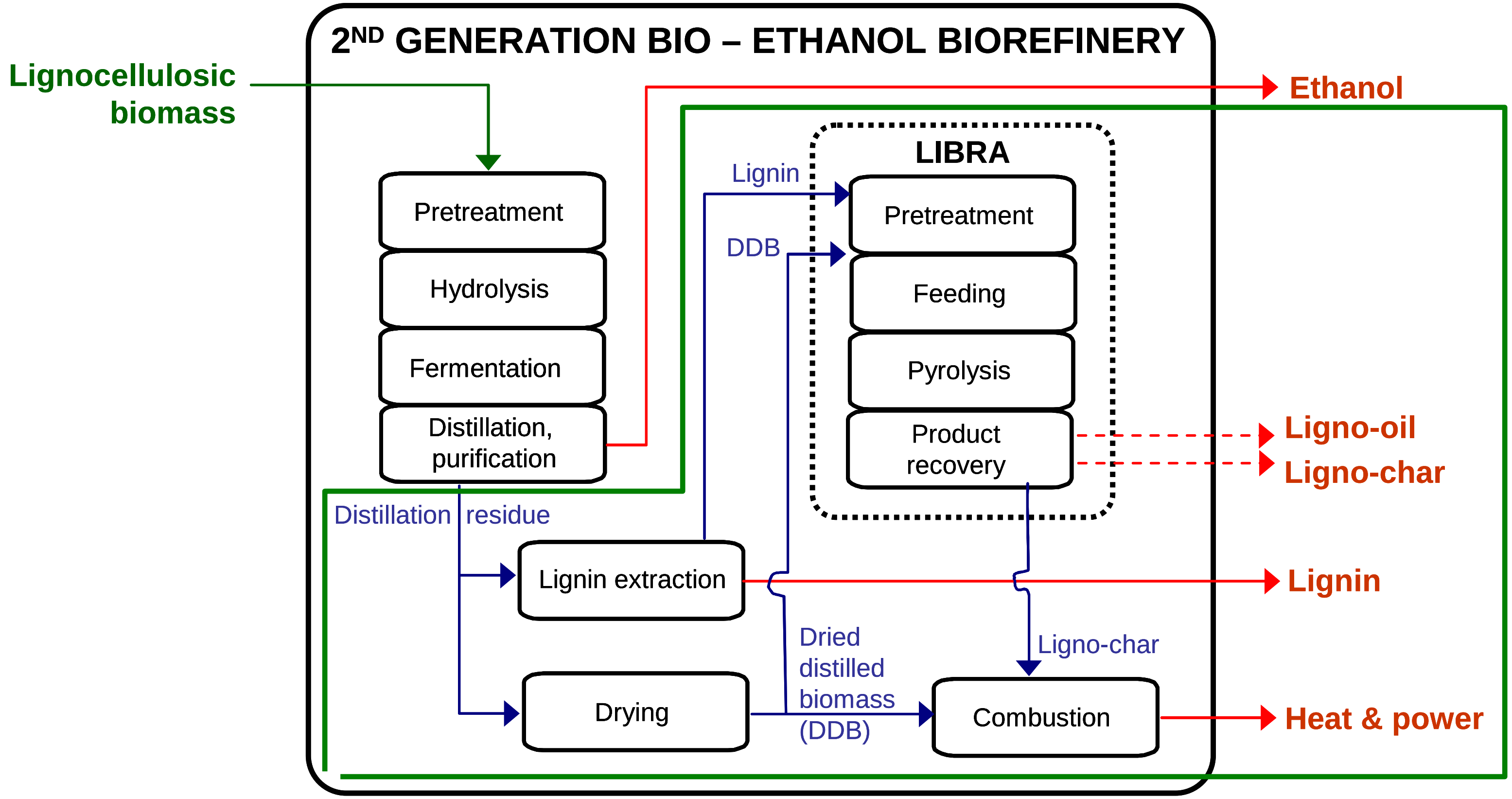
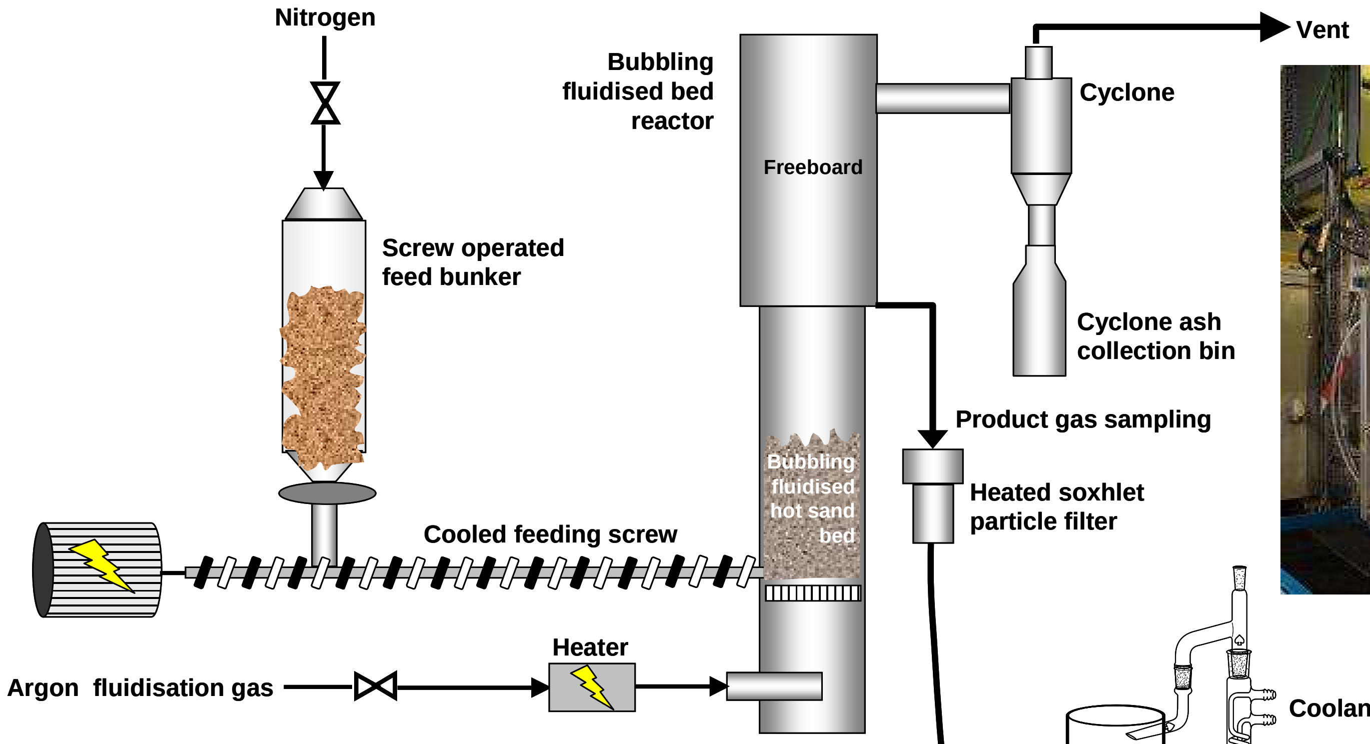
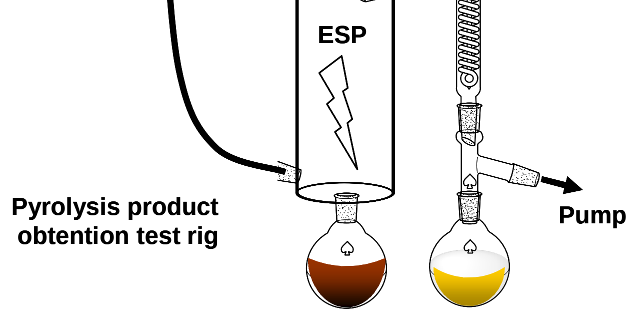


APPROACH

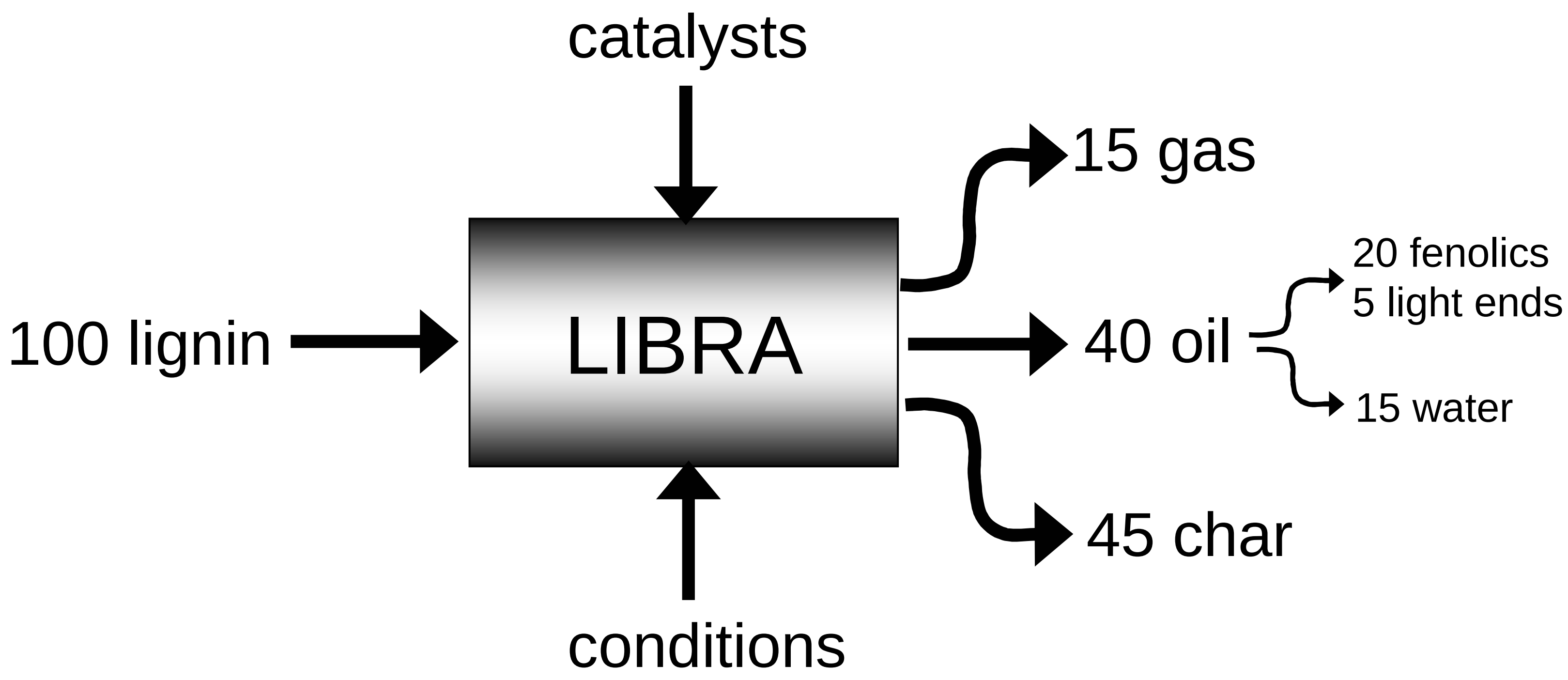
- Literature review / data assessment lignin pyrolysis
  - market analysis available lignins from both pulp & paper and biorefineries
  - analysis lignin pyrolysis processes, what process for what lignin?
  - market analysis lignin pyrolysis products (price & volume, manufacturers)
- Selection of one lignin variety and one pyrolysis process
  - estimation of mass balance of primary pyrolysis process
- Conceptual design lignin pyrolysis biorefinery, incl. product upgrading
  - process flow block scheme
  - simple Excel-model
- Detailed techno-economic modelling using ASPEN
- LCA





Bubbling fluidised bed pyrolysis test rig with collection of products

Lab-scale pyrolysis results ECN with Alcell lignin



CO-OPERATION TASKS 42 - 34

- TASK 42 input:
  Integration of a thermochemical lignin module in e.g. a 2nd generation bio-ethanol biorefinery
- TASK 34 input:
  Pyrolysis of lignin; design of a fast lignin pyrolysis unit on pilot scale
- ECN:
  Market studies and system evaluation (TEA & LCA)
- Time plan:
  - first concept summer 2010 (conceptual design)
  - TEA winter 2010 (ASPEN)
  - LCA spring 2011
- Dissemination as peer-reviewed paper (thesis chapter)