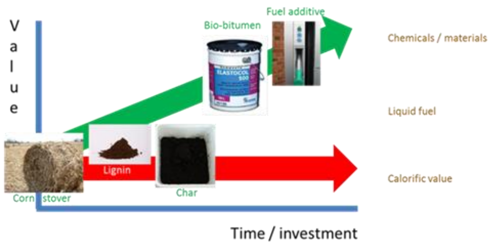

Agentschap NL
Ministerie van Economische Zaken

Public Final Report

1. Data project

- Project number: TEBE113004
- Project title: Lignin biorefinery to fuel additives, materials and energy; *LigniFAME*
- Secretariat and co-applicants: Progression Industry (Penholder)

Participant	Type of organization[1]	Role in project	Lead person(s)
Applicant Progression Industry (PI)	SME	Coordinator (supported by FBR), fuel additive application	Michael Boot, Jos Feijen
P1. Archer Daniels Midland Company (ADM Research)	Large company	Supplier of raw material, lignin from corn stover	Phil Hogan (formerly Jürgen Fisher)
P2. Wageningen UR Food & Biobased research (FBR)	Research organization	Lignin characterization, biomass fractionation, hydrothermal conversion and small-scale scCO2-assisted DSP, co-coordinator	Richard Gosselink, Hans Mooibroek,
P3. Energy research Centre of the Netherlands(ECN)	Research organization	Biomass and lignin characterisation, lignin isolation, lignin conversion, DSP, techno-economic analysis, screening LCA	Paul de Wild, Wouter Huijgen
P4. FeyeCon D&I BV	SME	Downstream processing of lignin oil fractions by using scCO2	Reyes Menéndez González, Audrey Ngomsik Fanselow
P5. Essent	Large company	Energy applications	Mark Bouwmeester, Karlijn Arkestein
P6. Soprema	Large company	Bio-bitumen applications	Remi Perrin, Nicky Horions

Project period: 01-01-2014 – 31-12-2015

2. Contents of public final report

Contents

3. Summary

To secure the future sustainable supply of energy resources, food and materials, full development and implementation of a more biobased economy is urgently needed.
In The Netherlands, besides food and feed applications, energy (electricity, heat and gas) is the largest market for the use of biomass. This is a (partly) policy driven market in which bioenergy has to provide a significant contribution to the overall Dutch sustainable Renewable Energy Policy goal of 16 % in 2020. In The Netherlands, co-firing of wood pellets in large power plants is one of the major technologies employed to reach this goal. In 2010 approximately 1.500 kiloton of wood pellets was being used for co-firing. As such, The Netherlands ranks third in Europe with regard to cofiring of biomass in power plants. In addition to the overall Dutch sustainable Renewable Energy Policy goal of 16 % in 2020, the Dutch Ministry of Economic affairs considers only options able to generate renewable energy at a base equivalent of 15 cent per kWh (or 103.53 cents / Nm^3) to be sustainable. Therefore, it is mandatory for the energy sector, as represented in this project by Essent as well as the biofuels sector (in this project represented by Progression Industry), to further drive down the costs for biomass use to be co-fired or to be used as biofuel, and to further develop innovative technologies to be able to achieve these goals. Within this project, the initial biomass caloric value will increase from 17 MJ / kg (~4.7 kWh/kg) to about 30 MJ /kg (~8.3 kWh/kg) for the residual char fraction as produced by thermochemical conversion of lignin.
The objective of this project was to demonstrate, at laboratory and pilot-scale, the feasibility of using lignocellulosic resources, which do not compete with food resources, for the sustainable production of energy (at a base equivalent of 15 cent per kWh (or 103.53 cents / Nm^3), energy carriers, fuel additives, materials and chemicals via cascading biorefinery concepts. In particular, lignin-rich biomass side-streams which are currently under-exploited were fractionated by novel technologies. The lignin part was converted and valorized into energy, energy carriers and materials. Based on criteria such as lignin content, availability, alternative uses, relevance for the biobased economy the partners in the project selected the following raw materials:

1. Corn stover which is widely available in Europe and US
2. Bamboo which is a fast growing lignocellulosic feedstock with a high lignin content
3. Softwood bark representing a side stream from the paper industry with a high lignin content
4. Sugar cane bagasse, which is a residue from sugar or ethanol production, was initially selected, but could not be sourced in time to the project

In this project the whole value chain starting from major producers of biomass side-streams (ADM), external suppliers of lignin-rich bamboo and softwood bark (from paper industry) via partners active in conversion and downstream processing of lignin fractions (FeyeCon, FBR, ECN, Progression Industry) to partners active in producing and marketing (end)products, energy, energy carriers, chemicals materials (Essent, ADM, Soprema, Maersk via Progression Industry) was covered.

Lignin containing biomasses were fractionated into their major fractions by two different technologies. The first acid hydrolysis fractionation by ADM and the second consisting of organosolv fractionation operated by ECN. The use of the carbohydrates part for conversion to cellulosic ethanol, biobased chemicals or paper applications was not studied in detail in this project. The focus of this project was on conversion of the isolated lignin part into marketable products via novel catalytic pyrolysis (ECN technology) and catalytic thermal conversion (FBR technology). Downstream processing by novel CO_2 extraction and vacuum distillation was studied to fractionate the liquid lignin fractions into the desired product mixtures. Additionally, bamboo was also used directly as input for a pyrolysis process. The different technologies led to different products such as gases and bio-char for energy application (performed by Essent and ECN), testing of liquid aromatics as base chemical and fuel additives (performed by Progression Industry), and testing of bio-char and lignin fractions for bio-bitumen for roofing application (performed by Soprema). The developed technologies and the resulting biorefinery concepts were further assessed by a first techno-economic analysis (ECN with input from all partners) and a screening LCA on its environmental aspects (ECN).

In the LigniFAME project the following achievements have been obtained:

The LigniFAME project showed that fractionation of lignocellulosic biomass (side) streams result in intermediate lignin products of sufficient purity and quality that can be used for the production of

energy carriers (char, fuel additives based on aromatics), material building blocks (lignin oligomeric fractions, char) and chemicals (aromatic monomers). By including higher value products derived from lignin the economic viability of a lignocellulosic biorefinery will certainly improve and subsequently biomass fractions can be used for cheaper energy production which met the overall goal of the project. In particular the pyrolysis technology using bamboo to generate lignin pyrolysis liquids was demonstrated at pilot scale. The resulting data were used for the preliminary techno-economic evaluation and LCA screening. For conversion of fractionated lignin either by pyrolysis, hydrothermal, or supercritical CO2 processing the production costs of lignin should become much lower than the anticipated costs of 500€/ton. This project however clearly showed the possibilities for the lignin conversion processes yielding several products such as gas, char, oil, and aromatics. The bamboo-derived char showed based on its basic properties co-firing potential.

The results from the industrial application trials with project samples (lignins, lignin oils, char) were at least partially successful and certainly merit further RTD along similar lines. LigninFAME clearly has established a firm stepping stone towards a higher technology readiness level (TRL) regarding valorisation of lignin and lignin-rich feedstocks (e.g. scale-up of the lignin production and pyrolysis processes).

Overall, the LigniFAME project has been successful and achieved all of its goals.

4. Introduction

Background and problem definition.

The growing world population is facing on one hand an increase in energy, food and material demand and on the other hand a growing production of greenhouse gases, pollution and an increasing dependency on fossil resources. To secure the sustainable supply of energy resources, food and materials, full development and implementation of a more biobased economy is urgently needed.
The European Union’s biomass market is regulated by the EU Climate and Energy Package (CEP) and the Renewable Energy Directive (RED). The CEP and the RED include an overall EU goal of 20% renewable energy consumption in 2020. In order to reach the individual Member States (MS) targets, the Dutch and Belgian governments imposed support programs for the energy sector. According the Dutch and Belgian Renewable Energy Action Plans (NREAPs) a major part of the renewable energy will be produced from biomass. Based on the NREAPs, FAS The Hague estimates that the Benelux wood pellet consumption will more than double during 2012 – 2020 to a volume of 5.7 MMT, representing a value of about US$ 1 billion. As domestic production is limited, the Benelux will mainly depend on imports, which are estimated to increase to about 5.5 MMT in 2020. Currently, the United States is the main supplier of wood pellets to the EU as well as to the Benelux market. In 2012, the United States is expected to export 1.25 MMT (US$ 225 million) of wood pellets to the Benelux (Flach, 2013).
In The Netherlands, besides food and feed applications, energy (electricity, heat and gas) is the largest market for the use of biomass. This is a policy driven market in which bioenergy has to provide a significant contribution to the overall Dutch sustainable Renewable Energy Policy goal of 16 % in 2020. In addition to this the Dutch Ministry of Economic affairs requires that only options, able to generate renewable energy at a base equivalent of 15 cent per kWh (or 103.53 cents / Nm^3), are considered to be sustainable. Therefore, it is mandatory for the energy sector (in this project represented by Essent as problem owner) to further develop innovative technologies, beyond the current co-firing of woody biomass options and first generation biofuels, to be able to achieve these goals. It is Essent’s vision that bio-refinery for higher value bio-products and biofuel, enables low cost bio-power production out of residues. Innovative biomass based technologies should ultimately create the possibility to substitute coal. For other industrial sectors, such as biomass suppliers (represented in this consortium by ADM) or major users of fossil based materials (Soprema), it is mandatory to develop innovative biomass based non-food technologies to ensure future business perspectives. Furthermore, it is necessary that biomass suppliers will have access to sufficient quantities of biomass to be relevant to energy, chemicals, and fuel producers.

5. Project structure

The project was composed of different work packages covering the whole value chain from biomass feedstocks, fractionation, conversion, downstream processing to application development and testing. The project contents are represented in the Figure 1.

Selected and up-graded lignin fractions were tested by the industrial partners (and research organizations) involved for the following application fields:
a) Energy (Essent, ECN): Energy from lignin-derived gas and char
b) Fuel additives (Progression Industry, ECN): CyclOx
c) Aromatic base chemicals (ADM): enhancing the value of corn stover-derived lignin and obtaining monomeric phenols for chemicals applications.
d) Bio-bitumen (Soprema): lignin-based raw materials (oils & bio-char) as raw materials into modified bitumen blends for roofing applications.

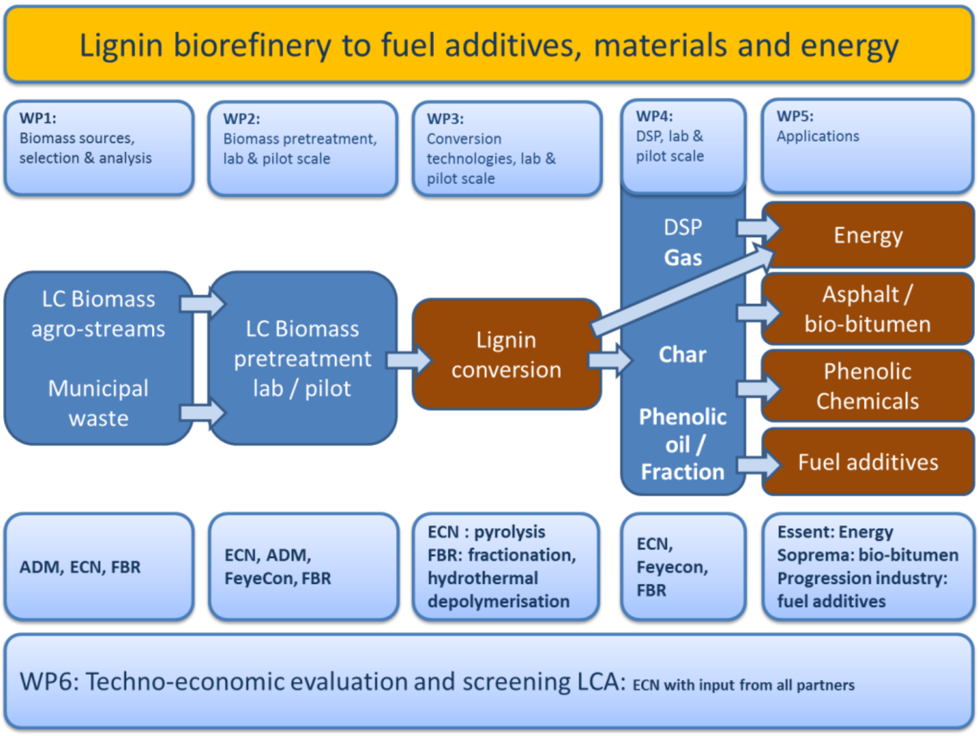

Figure 1: Project outline and work packages

6. Project results

The summative composition of the selected feedstocks was determined using standardized analysis protocols. Results are presented in Table 1.

Table 1: Composition LigniFAME lignocellulosic feedstocks (in wt% on dry mass)

Feedstock	Extractives		Hemicellulose					Cellulose	Lignin		Sum
	Water-soluble	EtOH-soluble	Xylan	Galac-tan	Arabi-nan	Mannan	Rham-nan	Glucan	AIL	ASL	
Bark *Picea abies*	25.1	4.2	2.7	1.3	1.7	3.5	0.3	24.7	22.3	0.7	92.2
Corn stover	10.7	2.6	19.3	0.9	2.1	ND	ND	33.9	15.4	1.5	94.4
Bamboo vulgaris	9.1	1.3	16.9	0.3	0.7	ND	ND	41.3	22.7	0.8	95.7

EtOH soluble = ethanol soluble extractives; AIL = Acid Insoluble Lignin; ASL = Acid Soluble Lignin; ND = not detected

The selected lignocellulosic feedstocks were successfully fractionated into pure lignin streams of minimum of 86% till 95% purity. The carbohydrate streams were considered for conversion by existing technologies into energy carriers (bio-ethanol or bio-butanol), chemicals, fibres, paper and materials. In this project the focus was on the lignin-rich streams for further conversion.

A scCO2 fractionation technology was used to further fractionate and depolymerize the purified lignins. The total conversion of lignin to phenolic compounds was at conditions (300°C and 270 bar) reaching 10% wt. total monophenol yield after two hours processing. The obtained yield was in the same range of those values found in the literature.

The thermal conversion of lignin was studied via catalytic pyrolysis and hydrothermal processes to find the optimal product distribution. Catalytic pyrolysis on lignin yielded up to 15% aromatic monomers and up to 30% of oligomeric lignin fragments. The char yield was about 30-40% and about 20% gases were formed. In addition, the lignin-rich feedstock bamboo was on processed on pilot (kg) scale via a specific slow-pyrolysis technique to produce a phenolic-rich bio-oil for evaluation as renewable bunker fuel and as ingredient for biobitumen. The overall mass balance was 94% (30% char, 46% oil, 17% gas).
Hydrothermal depolymerization of lignin leads to a strong depolymerization into a fraction of about 1200-1600g/mol after 4h and 900 g/mol after 24h and a yield of over 65wt%.
A limited amount of identified phenolic monomers was formed in the process (2,8%). Over time an increasing trend was seen in the alkylation process of the monomers. Also demethoxylation of phenolics was observed in the product mixture. Together the overall yield on monomers is about 15% based on lignin input. Residual lignin char yielded about 10% and a residual lignin fraction of about 15% was obtained.

Converted lignin fractions were upgraded via downstream processing technologies, such as primary fractions of the oily fractions, CO_2 supported extraction, and mild vacuum distillation into suitable lignin fractions for the applications. Staged condensation of the hot pyrolysis vapours was applied during the pyrolysis of the bamboo.

Selected and up-graded lignin fractions were tested by the industrial partners (and research organisations) involved for the following application fields:

a) **Energy**: the caloric values of the lignin-derived energy carriers gas and char were assessed for the required fuel properties for combustion in different power plants and the potential for heat integration at existing power plants. The bamboo-derived bio-char was evaluated for its co-firing possibility and eventual problems such as slagging and fouling effects. Based on a preliminary and limited assessment, the bamboo-char shows promise as co-firing material.

b) **Fuel additives**
- The lignin fractions and derived aromatic monomers were assessed to requisite fuel properties for CyclOx based biofuels. A biobased solvent was developed to solubilize the lignin and/or fractions to be used as fuel additive and successful lab-scale engine tests have been performed.

c) **Aromatic base chemicals**
Due to the complexity of lignin it seemed realistic to aim for bio-bitumen and fuel additives. The thermal technologies used in LigniFAME showed that from lignin a mixture of aromatic monomers can be produced in yield up to 15 wt%. In the pyrolysis process the monomers are of the phenolic type, while in the hydrothermal process also more alkylated phenolics are produced.

d) **Bio-bitumen**
Lignin derived oils & bio-char were tested into modified bitumen blends for roofing applications. These raw materials could be used either as partial substitute to current raw materials as bitumen and mineral filler or full substitute. Further studies are needed to optimise the lignin properties in a roofing membrane.

The screening LCA study shows that from an environmental point of view, bark is the most suitable option, but if transportation overseas is not taken into account, bamboo is a far better feedstock. From an availability point of view, bamboo might not be available worldwide, while bark could be. However,

presently most bark is converted into fuel pellets and as such not easily available for valorising via LigniFAME adapted technology routes such as organosolv fractionation and pyrolysis. Consequently, the valorisation of bamboo via (slow) pyrolysis was chosen for a further techno-economic / LCA analysis.
For the techno-economic evaluation the value chain consists of bamboo and its (pyrolysis) products (fuels, chemicals, performance materials) were used. The system boundaries are pretreatment → conversion → primary products → down-stream processing.
In conclusion, because of the low feedstock costs, simple conversion technology and product flexibility, slow pyrolysis of bamboo seems to be a viable valorisation option. The energy content of the non-condensable pyrolysis gas is sufficient to drive the process; with proper heat integration, autothermal operation is possible. From an empirical correlation, it appears that a 80 kton/a bamboo pyrolysis plant will cost ~30 M€. From an economic margin calculation the maximum revenue (excl CAPEX and OPEX) is estimated ranging from 2 M€/a (fuels) - 48 M€/a (bio bunker fuel and chemicals). Finally the maximum carbon-footprint for the pyrolysis process is ~16 kton/a when compared to ~146 kton/a in the case of bamboo as fuel.

7. Conclusions and recommendations

The LigniFAME project showed that fractionation of lignocellulosic biomass (side) streams result in intermediate lignin products which can be used for the production of energy carriers (char, fuel additives based on aromatics), material building blocks (lignin oligomeric fractions, char) and chemicals (aromatic monomers). By including higher value products derived from lignin the economic viability of a lignocellulosic biorefinery will certainly increase and subsequently biomass fractions can be used for cheaper energy production which met the overall goal of the project.
In particular the pyrolysis technology using bamboo to generate lignin pyrolysis liquids was demonstrated at pilot scale and used of the preliminary techno-economic evaluation and LCA screening results. For conversion of fractionated lignin either by pyrolysis, hydrothermal, or supercritical CO_2 processing the production costs of lignin should become much lower than the anticipated costs of 500€/ton. This project however clearly showed the possibilities for the lignin conversion processes in a spectrum of several products such as gas, char, oil, and aromatics. The bamboo-derived char showed based on its basic properties co-firing potential.

The results from the industrial application trials with project samples were at least partially successful and certainly merit further RTD along similar lines. LigniFAME clearly has established a firm stepping stone towards a higher technology readiness level (TRL) regarding valorisation of lignin and lignin-rich feedstocks (e.g. scale-up of the lignin production and pyrolysis processes).

This 2-years LigniFAME project should be considered as an initial phase towards further up-scaling and implementation during the subsequent phase. Future (R&D) activities are anticipated at the partners within the consortium, aiming at developing a full scale integrated biorefinery, using resources such as agro-side streams like corn stover and side-streams from paper production, softwood bark or a fast growing lignocellulose as bamboo. The intended output of such a biorefinery will be pyrolysis gas and bio-char for cheaper energy application, lignin and bio-char for roofing application, aromatic compounds as base chemicals and fuel additives in transport diesel applications.

Overall, the LigniFAME project has been successful and achieved all its goals.

8. Dissemination

LigniFAME results were presented at the following events:
- The Future of Aromatics' held on 13-14 January 2016 in Amsterdam (FBR)
- April 2015: "Bamboo pyrolysis for fuels, chemicals and energy" orally presented at the International Biomass Conference & Exposition" in Minneapolis, USA (ECN)
- September 2015: "BIORECOVER: BIOmass REsidues COnversion & Valorisation for an Economic Refinery" orally and visually (poster) presented at the Biorefinery-I conference in Crete (ECN)

- A peer-reviewed paper on the thermochemical conversion of corn stover lignin and/or bamboo will be submitted to the journal “Biomass & Bioenergy” (ECN)
- The results obtained from this project will be included in a Chapter in an upcoming book on biofuels, published by John Wiley and Sons “Biofuels from Lignocellulosic Biomass: Innovations beyond bioethanol”, edited by Michael Boot (Owner/Director PI).
- 2 patents are being prepared and will be submitted soon (PI).

9. Opportunities for spin-off and subsequent activities

Progression Industry will scale up the lab-scale knowledge gained in this project up to pilot scale in a recently granted OP ZUID / EU project (SceLio-4B). A second follow up project is planned to test various aromatic oxygenates as octane boosters in collaboration with a local race team.
Hydrothermal depolymerisation of lignin will be further developed within future project. The use of the Pd/C catalysts offer potential to introduce more selectivity in the aromatic product slate derived from lignin.
The pure organosolv lignins seem to be applicable to improve the characteristics of bitumen for roofing application which can be further investigated. It is expected that for bamboo direct harvesting, comminution, drying and slow pyrolysis on a medium scale in state-of-the art (rotating kiln-type of) reactors could pose an interesting, short-term economic activity for (developing world) regions with a surplus of bamboo, but lacking in energy and/or secondary energy carriers. A medium-term possibility is the catalytic pyrolysis of lignin, followed by scCO_2 extraction to produce phenolic fractions for various applications. A more long-term opportunity seems to be the recovery of high-value individual phenols from the complex phenolic mixtures after a pre-extraction with scCO_2. Even though more research is needed in order to optimize the process and to achieve selective extraction with high purity and increased yields, supercritical CO_2 technology has shown a great potential to be implemented in biorefinery downstream processing improving the profitability of the biorefinery and allowing the recovery of products of improved quality by using green and sustainable technology.
Finally, it has been discovered that the pyrolysis char, the carbonaceous residue from the pyrolysis activities, could actually be an interesting product with a higher added-value when compared to its value as a solid fuel. Applications such as filler material in roofing membrane were identified.

10. Contact

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11. Acknowledgements

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