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Valorisation of *Jatropha curcas* L. plant parts: Nut shell conversion to fast pyrolysis oil

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ABSTRACT

The biorefinery concept is a very powerful concept to optimise the conversion of biomass resources to value-added products with a minimum loss of energy and mass and a maximum overall value of the production chain. We here report our activities on the application of this concept to valorise the *Jatropha curcas* L. (JCL) shrub, a (sub)-tropical plant producing a high quality plant oil that may be converted to biodiesel in good yields. Within a research consortium of Dutch and Indonesian researchers, we are exploring high added value outlets for byproducts of the JCL plant (leaves, latex) and seed processing units (press cake). As an example, we here report fast pyrolysis experiments to convert the nut shells to fast pyrolysis oil, a promising second generation biofuel. The fast pyrolysis experiments were carried out in a continuous bench scale pyrolyser at a throughput of 2.27 kg/h at 480 °C and atmospheric pressure. The nut shell pyrolysis oil was obtained in 50 wt.% yield, the remainder being char (23 wt.%), gas (17 wt.%) and ash. Relevant product properties of the oil were determined and indicate that the oil is inhomogeneous in nature.

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1. Introduction

1.1. Possible applications of Jatropha curcas L. plant parts and processing residues

The *Jatropha curcas* L. (JCL) plant is currently receiving a great deal of attention (Kumar and Sharma, 2008; Openshaw, 2000; Achten et al., 2008). JCL has been recognised as a source for a medium viscosity pure plant oil (PPO) that is easily converted to biodiesel with good product properties (Agarwal, 2007). Both JCL PPO and biodiesel have been tested successfully in stationary diesel engines (Reddy and Ramesh, 2006; Achten et al., 2008). The growing global biodiesel market has attracted investors and project developers to consider JCL biodiesel as a substitute for fossil resources to reduce greenhouse gas emissions. The plant appears to have certain advantages compared to other (tropical) oil producing trees and plants. It has been mentioned that JCL is drought resistant and may grow at extreme conditions where other tropical plants and trees like the palm oil tree cannot survive or will produce unacceptable low yields of oil bearing fruits (Kumar and Sharma, 2008). In addition, the oil is toxic and as such JCL oil does not compete directly with food applications. This is of prime importance as the current first generation biofuels like biodiesel and bio-ethanol are derived from feedstocks that are also used in the food chain (various grains for bio-ethanol and pure plant oils for biodiesel). The food versus fuel discussion is still ongoing and puts serious pressure on the public acceptance of first generation biofuels (Srinivasan, 2009). A recent review expresses that JCL biodiesel certainly has potential but stresses that most claims on yields, simultaneous waste land reclamation capability and environmental impact are not from scientific literature and likely too optimistic (Achten et al., 2008).
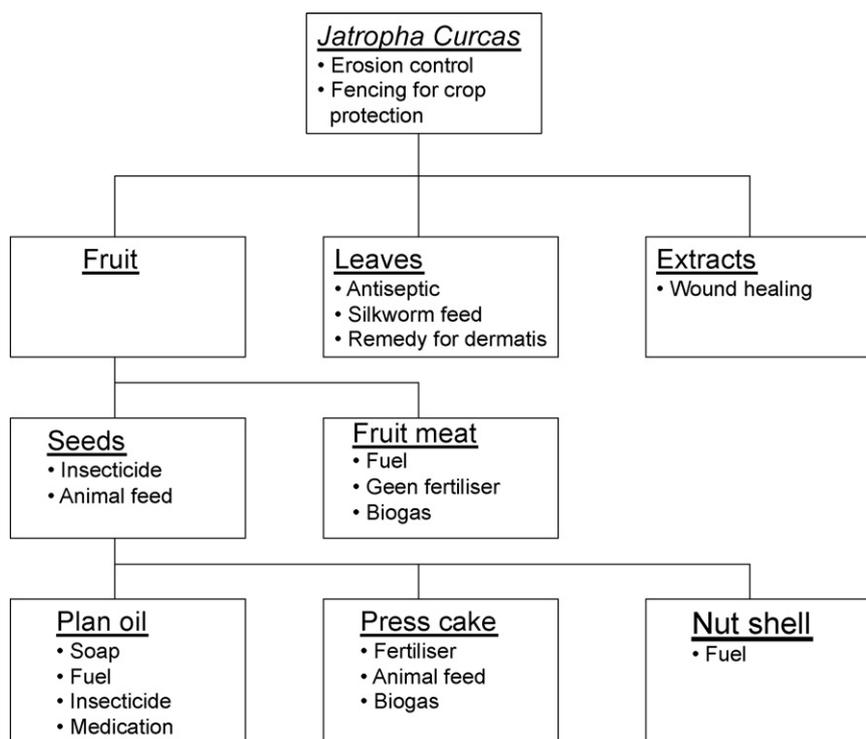
Fig. 1 – Possible applications of the *Jatropha curcas* L. plant.

Although the current focus of JCL valorisation is mainly on biofuels (PPO and biodiesel derived thereof), the plant produces many other potentially useful products (Kumar and Sharma, 2008). For instance, the fruit is rich in carbohydrates and could be applied for bio-ethanol production by fermentation (Demirbas, 2007). The seed cake, the residue after pressing the oil, may be used as animal feed (after detoxification), as a source of N-containing chemicals (Kumar and Sharma, 2008) or find industrial applications (adhesives) (Patel et al., 2008). The fibers may be applied as a binder in construction materials and various parts of the trees contain interesting components with pharmaceutical applications and can be of medicinal value. The shell of the seeds is rich in lignin and may be used for energy generation (Openshaw, 2000). An overview of possible applications mentioned in the literature is given in Fig. 1.

Evidently, there is a broad range of potential applications, products and associated markets available for the byproducts. Valorisation of these products is highly desirable for the following reasons:

- To increase the economic profit of the complete product chain.
- Without byproduct valorisation, large amounts of waste products will be produced at the processing units, leading to negative impacts on the environment.
- The products are made from green, renewable resources and fit with the trend towards the development of bio-based economies.

In 2006, a research team consisting of researchers from both Indonesia (Badan Pengkajian dan Penerapan Teknologi and the Institut Teknologi Bandung) and the Netherlands (Wageningen University and Research Center and the University of Groningen) started a 5-year project on the valorisation of JCL PPO and the byproducts of the JCL plant using the biorefinery concept. The team consists of 8 PhD students and supporting staff from both the Netherlands and Indonesia. In

the following, a short overview of the project will be provided. Subsequently, the research activities aimed at valorisation of the nut shells will be given. We will demonstrate that it is possible to convert the lignin rich nut shells into fast pyrolysis oil, which is considered a very attractive second generation biofuel.

1.2. The biorefinery concept

Biorefining aims at full valorisation of the biomass source by performing the overall processes with a minimum loss of energy and mass (Kamm et al., 2005; Clark and Deswarte, 2008). It consists of efficient fractionations/conversions of the biomass source into various value-added products and energy using physical separation processes in combination with (bio)-chemical and thermo-chemical conversion steps (Kamm et al., 2005). Large-scale biorefineries are operational already. Examples are the production of soy oil and soy protein from soy, wheat starch and gluten from wheat and potato starch and protein from potatoes. However, these existing biorefineries produce predominantly food products whereas the JCL biorefinery concept explored by our team has a strong focus on non-food applications. A possible biorefinery scheme for JCL is given in Fig. 2.

Within our Indonesian-Dutch JCL research team, a number of topics to valorise main- and byproducts are covered.

1.2.1. Optimisation of the production process for JCL oil
Traditionally, JCL oil is obtained by pressing the seeds of the plant. For a number of applications (for example biofuels), the oil needs further upgrading to meet the often stringent quality criteria. In this subproject, seed pressing technology is optimised, alternative oil recovery procedures are explored (for example enzyme assisted solvent extraction) (Latif et al., 2008) and process–product performance relations will be established. JCL PPO and the press cake are known to be toxic due to the presence of certain diterpenes and proteins (Makkar
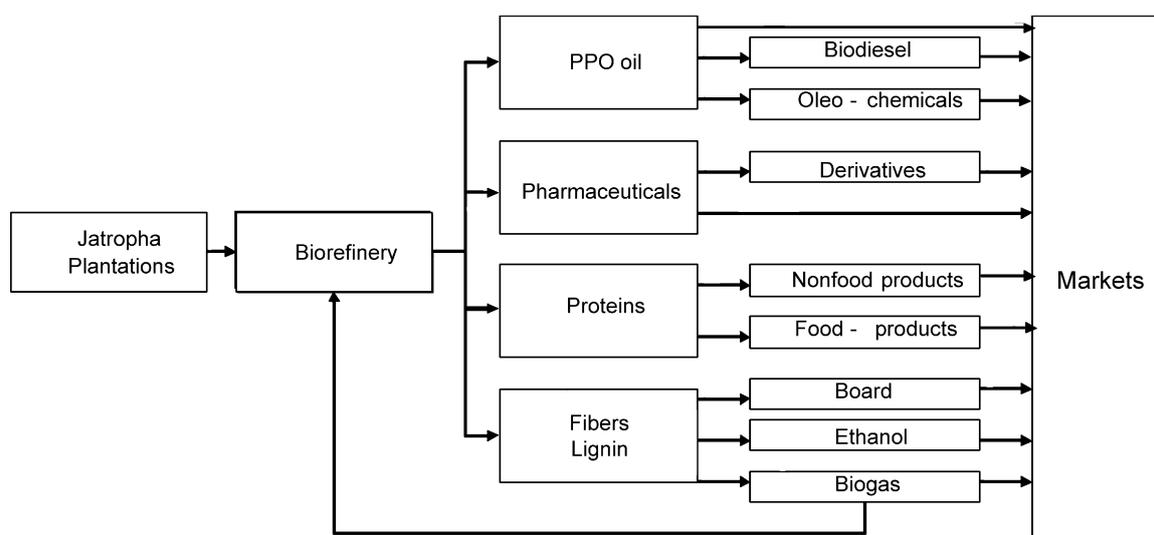
Fig. 2 – A possible biorefinery concept for JCL (simplified scheme).

et al., 1998; Achten et al., 2008). Particular attention will be given to the development of efficient detoxification procedures to allow for safe handling and to increase the value of the byproducts.

1.2.2. Development of interesting product outlets of JCL oil

An important and growing outlet for plant oils is the conversion to biodiesel by transesterification with methanol and a basic catalyst (Agarwal, 2007). This leads to improved product properties. For example, the viscosity is reduced considerably which has a positive effect on engine performance. We are exploring alternative catalytic concepts to lower the viscosity of JCL PPO, for example by the application of catalytic metathesis reactions of the PPO with olefinic substrates like ethylene (Rybak et al., 2008).

Natural oils are also important building blocks for the (oleo-) chemical industry (Kamm et al., 2005; Clark and Deswarte, 2008). Catalytic technology to prepare epoxidized JCL oil is explored within the project. This compound could be an attractive building block for derivatives that may find applications as biolubricants, reactive thermosetting resins and as plasticizers for PVC. In a second project, pharmaceutically interesting compounds from the oil will be identified and their medicinal value and potential to be used as chiral synthons for high value-added pharmaceuticals will be explored.

1.2.3. Exploration of attractive technology to valorise byproducts

Byproducts such as the press cake from the seeds, the fruit bodies as well as the leaves of the plant offer additional opportunities for interesting product outlets (Openshaw, 2000; Kumar and Sharma, 2008). Examples are the applications of the press cake proteins as a source of animal feed (after detoxification) (Haas and Mittelbach, 2000) and/or industrial applications like glues, coatings and films (Patel et al., 2008). Improved isolation procedures for protein recovery are explored within the project. The lignin as well as the fibers may be applied for making construction materials whereas the carbohydrates could be applied as a source for bio-ethanol (Demirbas, 2007). These topics are also covered within the project.

1.3. Fast pyrolysis technology

In this paper, the use of fast pyrolysis technology to valorise the JCL nut shell is discussed. This paragraph gives some insight in fast pyrolysis technology and product properties of the resulting fast pyrolysis oils. It is not intended as a comprehensive review, for this the reader is referred to recent reviews in the field (Digman et al., 2009; Babu, 2008; Qi et al., 2007; Mohan et al., 2006). Fast pyrolysis is a promising conversion technology for lignocellulosic biomass (Bridgwater et al., 1999). It is a medium temperature process (400–500 °C) in which the biomass feedstock is thermally degraded in the absence of air/oxygen to solids (charcoal), liquids (fast pyrolysis oil) and gaseous products. The fast pyrolysis oil is considered a very attractive second generation biofuel. It has a higher energy density than the solid biomass source and can be transported more easily. Typical liquid product yields are a function of the feedstock, processing conditions and equipment and may be up to 80 wt.% on dry biomass. Char (10–20 wt.%) and combustible gases (10–30 wt.%) are the major byproducts. The char (biochar) is currently receiving a lot of attention as it has good potential for soil improvement (Gaunt and Lehmann, 2008). The gasphase generally consists mainly of CO, CO_2 and H_2 and may either be used for energy generation or for the synthesis of (bulk)-chemicals (for example methanol and FT-diesel) (Bridgwater et al., 1999).

Many different types of pyrolysis reactor configurations have been developed over the last decades (Bridgwater et al., 1999; Zhang et al., 2009). Examples include fluidized beds, transported and circulating fluidized beds, spouted beds, ablative and vacuum pyrolysis. Recent developments include microwave assisted pyrolysis (Huang et al., 2008) and plasma pyrolysis (Huang and Tang, 2007).

A process scheme for a typical pyrolysis process is provided in Fig. 3. The biomass is fed to the reactor where it is rapidly heated (<2 s) by hot sand. The vapour phase leaving the pyrolysis reactor is cooled in a quencher with cold fast-pyrolysis oil. The condensable fast pyrolysis liquids are collected. The char and the sand are transported to a combustor, where the char is combusted with air to generate heat for the endothermic pyrolysis process. The hot sand is recycled to the reactor.

Developments in fast pyrolysis technology have been impressive and the process is now close to full-scale com-
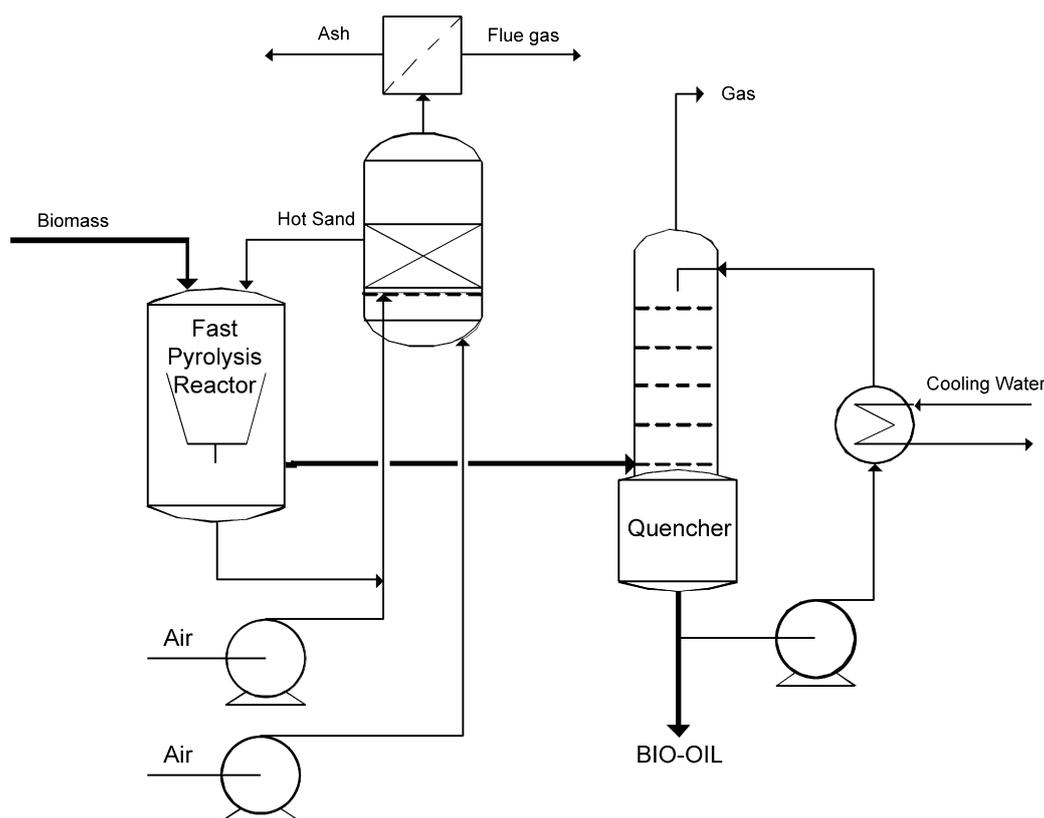
Fig. 3 – Process flow diagram of BTG's fast pyrolysis process of biomass (Courtesy of BTG B.V.).

mercialization. To the best of our knowledge, the largest two plants constructed to date are a 2000 kg/h unit of BTG/Genting in Sanyen, Malaysia in 2005 (www.btgworld.com) and an 8000 kg/h Dynamotive Plant in Canada (Bridgwater et al., 1999). The biomass feedstock for the BTG/Genting plant consists of empty fruit bunches from the palm oil industry. Recently, Dynamotive announced plans for the construction of a 200 ton/day fast pyrolysis plant in the US using saw dust as the feedstock (www.dynamotive.com).

Fast pyrolysis is a very versatile technology with respect to feedstock and a wide variety of biomass has been pyrolysed successfully (Mohan et al., 2006). Examples include residues from the wood industry and agricultural waste products. Waste biomass sources with a high potential include bagasse, rice husk, rice straw, switchgrass, wheat straw and empty fruit bunches of the palm oil industry (Bridgwater, 2003).

To the best of our knowledge, the use of the JCL nut shells as a feedstock for a fast pyrolysis process has not been explored to date. Pyrolysis technology has been applied for valorisation of the residue of JCL after oil extraction (Sricharoenchaikul et al., 2008). This material (press cake) is a mixture of kernel material and shells with residual amounts of PPO. In this case, slow pyrolysis ($T = 400$–$800\,^\circ$C, hold times > 15 min) was applied with the aim to produce porous char. Activated carbons with high surface areas were subsequently obtained by treatment of the pyrolysis char with concentrated KOH or H_3PO_4. The same group also explored the thermal decomposition characteristic of JCL press cake using thermogravimetric analyses (Sricharoenchaikul and Atong, 2007). Effects of heating rate (5–90 $^\circ$C/min), reaction temperature (500–900 $^\circ$C), and hold time at final temperature (3–15 min) on the thermograms, kinetic parameters as well as product distribution were evaluated.

Fast pyrolysis oil, also known as bio-oil, is a dark brown liquid with a pungent odour. The higher heating value (HHV) is about 16–19 MJ/kg, which is about half of crude fossil oil (42 MJ/kg) (Bridgwater et al., 1999). However, fast pyrolysis oil contains less ash and is easier to transport than the original solid biomass source. Some important product properties of fast pyrolysis oil are shown in Table 1. The product is rather acidic, contains significant amounts of water and bound oxygen and has a relatively high viscosity. Upon storage, the oil tends to phase separate, although effective measures have been developed to circumvent this issue (for example by alcohol addition) (Mohan et al., 2006).

Fast pyrolysis oil contains up to a thousand of different chemical components that may be classified according to functional groups. Typical compound classes are organic acids, aldehydes, ketones, phenolics and alcohols (Diebold, 2000).

Table 1 – Typical properties of wood derived fast pyrolysis oil (Bridgwater et al., 1999).	
Properties	Typical value
Water content (wt.%)	15–30
pH	2.5
Specific gravity (kg/l)	1.2
Elemental analysis, dry basis (wt.%)	
C	54–58
H	5.5–7.0
O (by difference)	35–40
N	0–0.2
Ash	0–0.2
HHV as produced (25% water content, MJ/kg)	16–19
Viscosity (at 40 $^\circ$C and 25% water, cP)	40–100
Solid (char, wt.%)	0.2–1.0

An immediate application of fast pyrolysis oil is energy generation. Research has been conducted on the use of the oil in boilers, gas turbines and large diesel engines for electricity generation (Bridgwater et al., 1999). Recently, co-feeding of the pyrolysis oil to a gas fired power station of Electrabel in Harculo has been succesfully demonstrated (www.btgwold.com). Pyrolysis is also gaining increasing importance as a pretreatment step for gasification or combustion processes (Babu, 2008).

Another interesting application is the use of the oil as a source for chemicals. The oil contains various oxygen containing, high added value compounds (Diebold, 2000). Examples are hydroxyacetaldehyde (glycolaldehyde), the smallest sugar molecule, acetol and organic acids like acetic acid and formic acid. Levoglucosan is an interesting sugar derivative that can be isolated relatively easily from the oil. The pyrolysis oil contains various low molecular weight phenolics arising from breakdown of the lignin part of the ligno-cellulosic biomass during pyrolysis. These may find applications in the wood adhesive industry as a (partial) replacement of phenol in phenol-formaldehyde and related resins (Kamm et al., 2005; Effendi et al., 2008).

2. Experimental

2.1. Materials

The JCL seeds were obtained from a plantation near Bandung, Indonesia. The nut shells were manually removed from the seed. The shells were ground in a DFH048 grinder.

2.2. Analytical methods

2.2.1. Ash content of the nut shells
The nut shells were first dried overnight at 105 °C. Samples of the dried feedstock were then weighed and placed in an oven at 550 °C. After about 8 h the sample was cooled down to room temperature. Before the amount of ash was weighed, the sample was again dried at 105 °C for 24 h to remove any moisture obtained from the air during cooling. The analyses were performed in triplicate, which resulted in a relative error below 1%.

2.2.2. Elemental composition
The elemental composition of the fast pyrolysis oils and the nut shells (C, H and N) were determined using an Euro Vector 3400 CHN-S analyser. The oxygen content was determined by difference. The reported values are the average of two independent analyses.

2.2.3. Determination of the metal composition of the recycle sand
The metal composition was determined using inductively coupled plasma (ICP). Samples were heated in an oven at 550 °C until they were reduced to ash. The resulting ash was dissolved in a 2 wt.% HNO_3 solution and measured by ICP.

2.2.4. Determination of the water content of fast pyrolysis oil samples
The water content of the pyrolysis oil samples was determined using a Karl-Fischer titration (702 SM Titrino, Metro-Ohm). The samples were dissolved in Hydranal solvent (Riedel-de-Haen) and titrated using Hydranal Composite 5 (Riedel-de-Haen).

2.2.5. NMR analyses
^1H NMR spectra were recorded on a 200 MHz NMR (AMS100, Varian). The samples were dissolved in $CDCl_3$.

2.2.6. Viscosity measurements
The viscosity was measured using a Brookfield viscosity meter using spindle RV 6. The viscosity was measured at 22.4 °C for 10 min at a shear rate of $1.67 \, s^{-1}$.

2.2.7. pH measurements
The pH of each sample was measured using a 691 pH meter from Metrohm.

2.3. Flash pyrolysis experiments

Before a pyrolysis experiment, the shells were dried to a moisture content of 4.7 wt.% using an electrical oven at 105 °C. The feeding system of the pyrolysis unit was calibrated using the dried JCL shells to determine the pre-determined input feed rate. During these calibration tests the shells were processed through the feeding section, which resulted in grinding of the shells. The average particle size of the shells was thus reduced within the system to an approximate size of 1 mm. The flash pyrolysis experiments of the JCL nut shell were carried out in a continuous flash pyrolyser with a maximum throughput of 5 kg/h using rotating cone technology (Fig. 4).

The experiments were carried out at atmospheric pressure with a typical feeding rate of 2.27 kg/h and a pre-set pyrolyser temperature of 450 °C. The experiment was run for 80 min. The actual reactor sand in- and outlet temperatures were 492 and 472 °C, respectively. The reactor temperature was higher than the pre-set temperature of 450 °C. This is likely due to the formation of relatively high amounts of char which is known to lead to higher combustion temperatures. The actual combustor temperature was 563 °C. The pyrolysis vapours were liquefied in two successive condensers (1 and 2) at temperatures around 40 °C (Fig. 4). Cooling was performed by spraying the vapours with cold fast pyrolysis oil. At the start-up of the process, both condensers were partly filled with a start-up oil, in this case fresh pine wood pyrolysis oil. During the experiments, various oil fractions were collected in both condensers 1 and 2. The fractions were analysed and weighted for mass balance calculations. The char yield was determined indirectly, because the char is burned inside the combustor to generate the heat required for the endothermic pyrolysis process. The amount of oxygen required for combustion was determined by measuring the oxygen content of the flue gas. Based on the oxygen balance the amount of char which is combusted can be calculated.

3. Results and discussion

The JCL seeds consist of a hard black nut shell and a soft white kernel containing the plant oil in a protein rich matrix. Typically the shells represent about 48 wt.% of the total nut (Sirisomboon et al., 2007). With an estimated nut production of 2 ton/(ha year) (Achten et al., 2008) this corresponds to a production of about 1 ton of nut shells per hectare per year. Thus, identification of higher added value outlets for the nut shell is worthwhile and deserves further attention. In the following the chemical composition will be discussed and the application of the nut shells as a feedstock for fast pyrolysis will be explored.
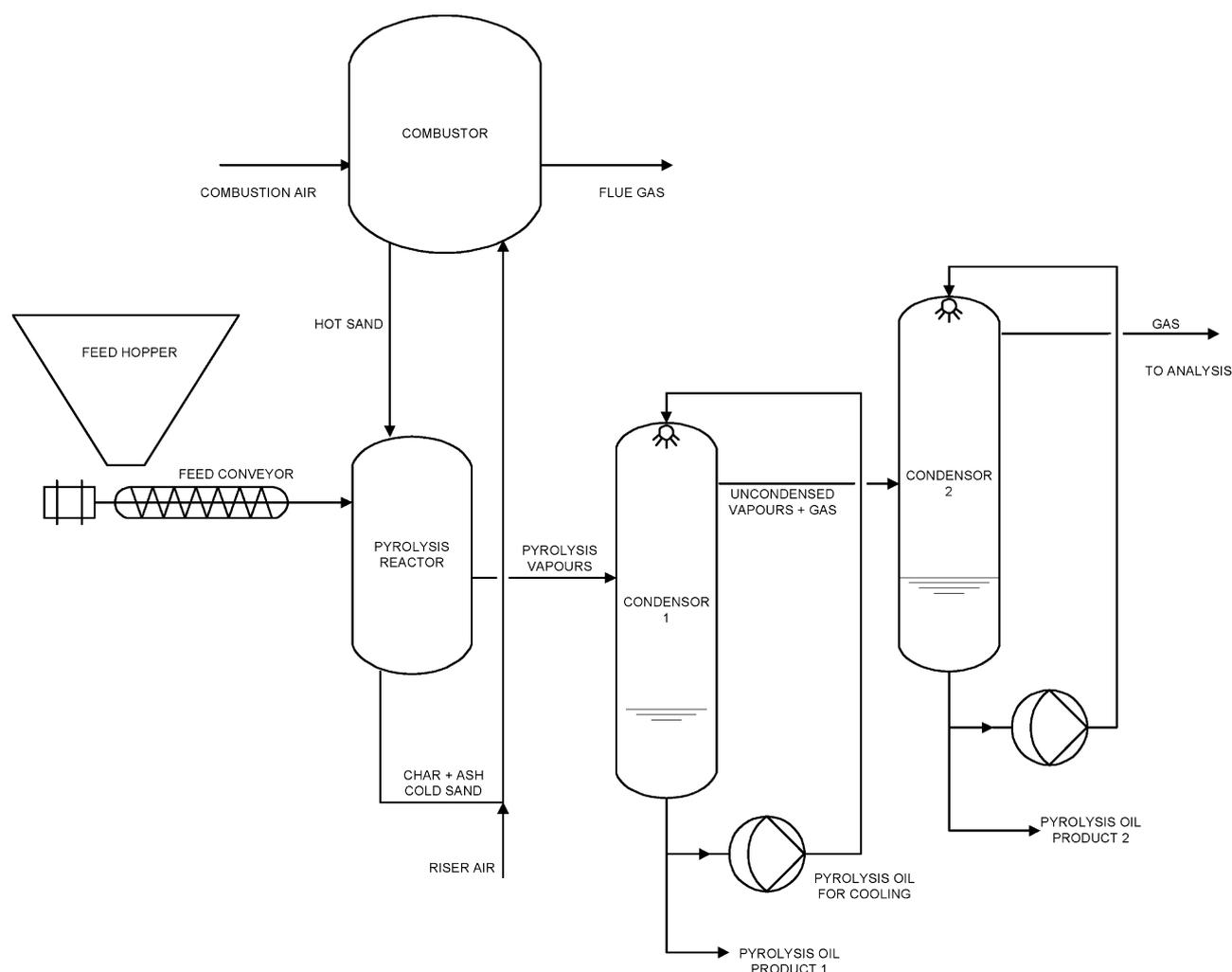
Fig. 4 – Schematic representation of the bench scale flash pyrolysis set-up used in this study.

3.1.　*Chemical composition of the nut shell*

The water content and the elemental composition of the nut shells were determined. The water content of the nut shells was 11.0 wt.%. This value is close to literature data 8.1–10.2 wt.% (Makkar et al., 1998) and 9.1 wt.% (Wever et al.,

submitted for publication). Before pyrolysis, the feedstock was oven dried at 105 °C to reduce the moisture content. This facilitates processing and improves the quality of the resulting product oil. The moisture content after drying was 4.7 wt.%.

The elemental composition of the nut shells was determined by elemental analysis and the results are given in

Table 2 – Elemental composition of the JCL nut shell.[a].						
	C	H	O	N	S	Ash
This study	50.3	6.6	38.3[b]	1.8	n.d.[c]	3.0
Literature (Wever et al., submitted for publication)	48.5	5.7	41.0	0.67	<0.01	4.08[d]

[a] In wt.% on wet basis.
[b] By difference.
[c] Not determined.
[d] By difference.

Table 3 – Overview of oil fractions collected during a representative pyrolysis experiment.				
Pyrolysis oil details	Condenser 1 (main product)		Condenser 2 (balance closure)	
	Mass (kg)	Moisture (wt.%)[a]	Mass (kg)	Moisture (wt.%)[a]
Start-up oil (pine oil)	0.655	22.0	0.3830	22.0
Fraction 1	0.700	28	0.1847	21.7
Fraction 2	0.513	33	0.3422	21.0
Fraction 3	0.833	33	–	–

[a] Measured directly after production.

Table 4 – Mass balance for the fast pyrolysis process of JCL nut shell.	
Mass balance	Amount (wt.%)
Oil yield	50
Gas yield	17
Char yield	23
Ash 'yield'	3
Balance closure	93

Table 2. Of interest is the N-content, which is higher than reported in the literature. This difference is likely due to the presence of residual amounts of white kernel material in our samples, which is known to be rich in proteins (Makkar et al., 1998).

The ash content, an important input parameter for fast pyrolysis, was 3.0 wt.%. This value is in line with literature data (2.1–6 wt.%, depending on the variety) (Makkar et al., 1998). Wever et al. also determined the contents of the main constituents (cellulose, hemicellulose and lignin) of the nut shell and found that the shell is relatively rich in lignin (47.6 wt.%). Typically, lignin values for softwood biomass are between 23–33 and 16–25 wt.% for hard wood biomass (Mohan et al., 2008). The values for cellulose and hemi-cellulose were 22.3 and 23.8 wt.%, respectively. The hemi-cellulose fraction is at the low end for woody biomass (25–35 wt.%), whereas the cellulose content is considerably lower than found for woody biomass (40–50 wt.%). Thus, it can be concluded that the nut shell is relatively rich in lignin and contains relatively low amounts of cellulose. This is expected to have a profound effect on the composition and properties of the resulting fast pyrolysis oil.

3.2. Fast pyrolysis experiments

The fast pyrolysis experiments of the JCL nut shell were carried out in a continuous flash pyrolyser with a maximum throughput of 5 kg/h using rotating cone technology (Fig. 4). An overview of the number and amount of the various oil fractions collected during a representative run is provided in Table 3. The first fraction was highly diluted with the start-up oil and not representative for the JCL nut shell oil.

Besides the dark brown pyrolysis oil, non-condensable gases and char were produced as well. The mass balance for the complete process is given in Table 4. Mass balance closure is acceptable (93%).

The oil yield was 50 wt.%. Typical pyrolysis oil yields are between 40 and 65 wt.% on dry feed depending on feedstock composition, process conditions and processing equipment (Bridgwater et al., 1999). Thus, the liquid yields obtained for the JCL nut shell are at the low end of the reported values. It

is well established that feedstocks high in lignin, such as bark and olive husk, have the tendency to give relatively low oil yields (Mohan et al., 2006). It should be realised that the experiments reported here are the proof of principle only, and further yield improvements are possible by process optimisation (e.g. reactor temperature, particle sizes, heating rates).

### 3.3. Properties and elemental composition of the fast pyrolysis oil, gas and char

3.3.1. Fast pyrolysis oil properties and composition
The fast pyrolysis oil was isolated as a dark brown viscous liquid with a typical pungent odour. Initially the oil was free of visible solid particles, however, after 1 month storage at 4 °C, the formation of a small amount of solid material on the bottom of the storage container was observed. Determination of the water content of the samples resulted in a large spread of values, even within a specific oil fraction (1–3 in Table 3). One of the possibilities for this phenomenon is the occurrence of phase separation upon storage and the formation of two discrete liquid phases (Diebold, 2000). However, this was visually not observed. An alternative explanation is the occurrence of concentration gradients within a sample. To proof this hypothesis, fraction 3 (stored for 1 month at 4 °C) was allowed to settle for 24 h at room temperature and subsequently samples of the top, middle and bottom part of the container were taken and analysed (elemental composition, pH, water content, viscosity, ^{1}H NMR). The data are given in Table 5, representative ^{1}H NMR spectra of the various samples are given in Fig. 5. The pH value of all samples was 3.3–3.4, indicative for the presence of organic acids. The water content, elemental analyses and ^{1}H NMR spectra clearly show the presence of concentration gradients in the sample and indicate that the pyrolysis oil is inhomogeneous in nature. The analytical data for the top sample suggest that it is rich in a pure plant oil. The C and H content are high for a typical pyrolysis oil and closer to those found for pure plant oils. An ^{1}H NMR spectrum of the top sample (Fig. 5) confirms this statement and shows characteristic resonances of the fatty ester chains of a typical PPO (δ 0.8 ppm (CH$_3$), δ 1.3 ppm (CH$_2$), δ 5.4 ppm (C=CH)). The ^{1}H NMR spectrum of the bottom fraction is distinctly different and clear resonances of the fatty acid chains of PPO are absent. Clearly visible are resonances of aldehydes and organic acids (δ 8–10 ppm), aromatic protons (δ 6.4–8 ppm), methoxy groups (δ 3–4.2 ppm) and aliphatic methyl and CH$_2$ groups (δ 0–2.2 ppm), in line with typical data for pyrolysis oils (Ingramm et al., 2008). On the basis of these analyses, it can be concluded that the oils are inhomogeneous and are likely intermediate between a homogeneous and a fully phase separated oil.

The PPO in the oil likely originates from the presence of white kernel material in the nut shell pyrolysis feed due to

Table 5 – Elemental composition and selected product properties of the top, middle and bottom samples taken from fraction 3.			
Product property	Top sample	Middle sample	Bottom sample
pH	3.3	3.3	3.4
Water content (wt.%)	23.3	23.9	55.3
Viscosity (mPa s)	270	100	30
Elemental composition (wt.%)			
C	65.6	27.8	31.0
H	9.5	8.8	8.7
N	0.9	1.0	1.1
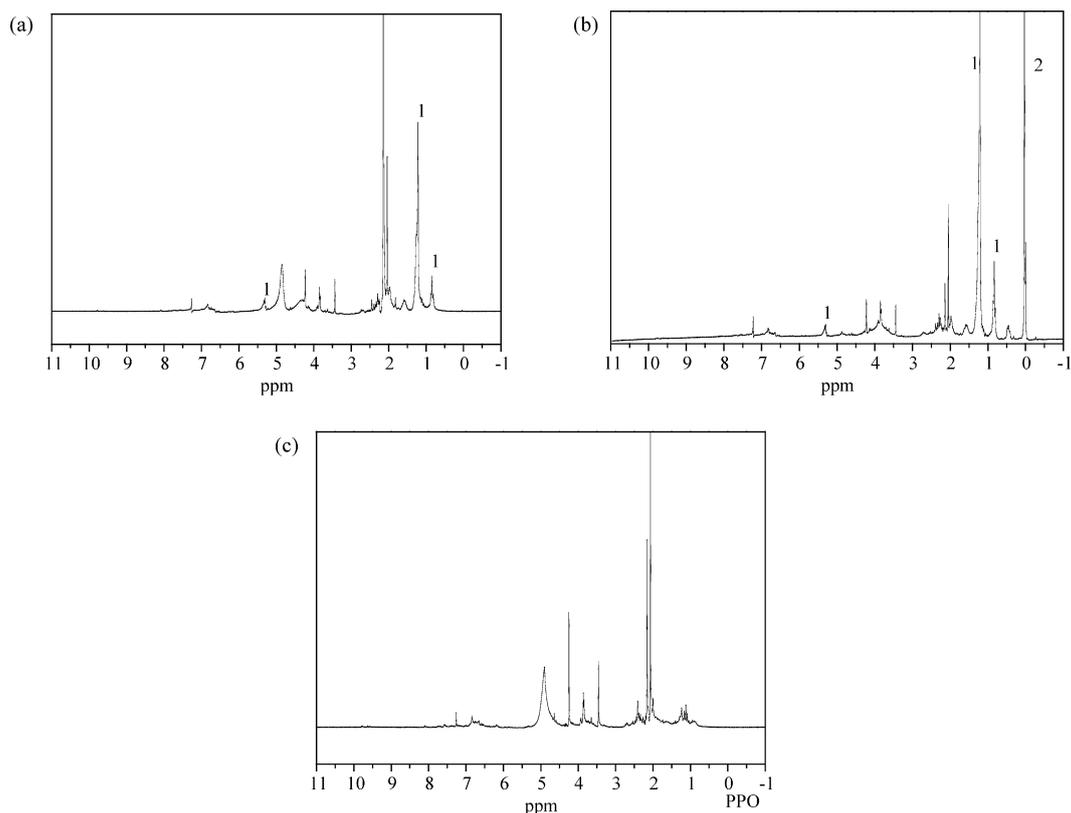
Fig. 5 – ^1H NMR spectra of top (a), middle (b) and bottom (c) sample. (1) Main peaks from PPO; (2) internal standard (tetramethylsilane, TMS). Peak at δ 7.21 ppm is from the NMR solvent ($CDCl_3$). All other peaks are from the various components within a typical pyrolysis oil.

Table 6 – Composition of the non-condensable gases in the outlet of condenser 2.

Component	As measured (vol.%)	Corrected for N_2 (vol.%)
N_2	40.3	0
CO	21.4	36.5
CO_2	30.5	51.9
CH_4	5.2	8.9
C_2+	1.5	2.6

Table 7 – CHN analyses of the solids.

Element	Amount (wt.%)
C	10.8
H	0.58
N	0.47

incomplete manual separation. The white kernel is known to be rich in proteins and pure plant oil. This hypothesis is confirmed by visual observations and elemental analyses on the nut shell pyrolysis feedstock. It shows a higher N-content compared to literature data (*vide supra*) and is thus indicative for the presence of proteins arising from residual kernel material.

3.3.2. Composition of the pyrolysis-gas
During the fast pyrolysis process part of the feedstock is transformed into non-condensable gases. The composition of the outlet gases was analysed with online GC. The composition of the gas in the outlet of condenser 2 (Fig. 4) is presented in Table 6. The main component is CO_2, followed by CO and methane. Hydrogen could not be detected. Furthermore, the gas contains 40 vol.% of nitrogen. Nitrogen gas is deliberately fed to the pyrolysis system to act as a purge flow to protect certain instruments. For large-scale pyrolysis the amount of nitrogen fed to the pyrolyser is considerably lower, therefore the gas composition is also recalculated on a nitrogen free basis.

3.3.3. Composition of combustor sand and pyrolysis-char
The char produced in the pyrolysis reaction is together with the recycle sand transported from the pyrolysis reactor to the combustor (Fig. 4). Here it is burned with an air stream to heat up the sand before it is returned to the pyrolyser. Thus it is not possible to analyse the composition of the combustor sand and char directly. However, parts of the solids in the combustor are entrained, end up in the off-gas cyclone and may be collected (Fig. 4). Analysis shows that the entrained solids contain about 10 wt.% unburned char and 90 wt.% of ash. The solid fraction was further analysed by elemental analyses (C, H, N) and ICP. The data are given in Tables 7 and 8.

Table 8 – Metal analyses for entrained and virgin combustor sand.

Element	Virgin combustor sand (ppm)	Entrained combustor sand (ppm)
Al	1440	9100
Fe	340	4420
Na	139	540
Ca	1000	45000
Mg	80	12200
P	<1	11000

The ICP analyses indicate that the entrained combustor sand is enriched in metals like Al, Fe, Na, Ca, as well as in P. This confirms that the inorganic ash in the biomass for a large part ends up in the combustor solids and accumulates in the sand recycle in the system. In commercial operation, recycle sand bleeding is required to avoid excessive accumulation of ash in the sand recycle stream. The data clearly indicate that the recycle sand is enriched in important plant nutrients (P, N, Ca, Mg) and has potential to be used as a fertiliser.

4. Conclusions and outlook

In this paper we have provided the proof of principle for the conversion of JCL nut shells by a fast pyrolysis process to pyrolysis oil. The experiments were carried out in a continuous bench scale rotating cone fast pyrolyser at 470–490 °C and atmospheric pressure. The non-optimised pyrolysis oil yield was 50 wt.%, the remainder being char (23 wt.%) and gases (17 wt.%). Relevant properties of the pyrolysis oil were determined. It was demonstrated that the oil is inhomogeneous with both a water and PPO gradient. The PPO likely originates from the presence of residual seed kernel in the nut shell feedstock.

Fast pyrolysis may become an essential element in JCL biorefineries to valorise the nut shells into fast pyrolysis oil, a promising second generation biofuel. The pyrolysis process is highly flexible in feedstock, implying that other residues (leaves, wood) from the plantations may be valorised as well. The resulting pyrolysis oil may either be used on site for energy generation in for example boilers or transported to larger facilities for further upgrading to for example liquid transportation fuels. Furthermore, the pyrolysis process also produces a char–sand mixture which is rich in minerals and has potential as a soil improver (biochar). The gaseous components may be used for energy generation or bulk chemicals synthesis.

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