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Research Article

Keywords: Bioenergy, environment, pinedust, pyrolysis, sustainability

Posted Date: February 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-178419/v1>

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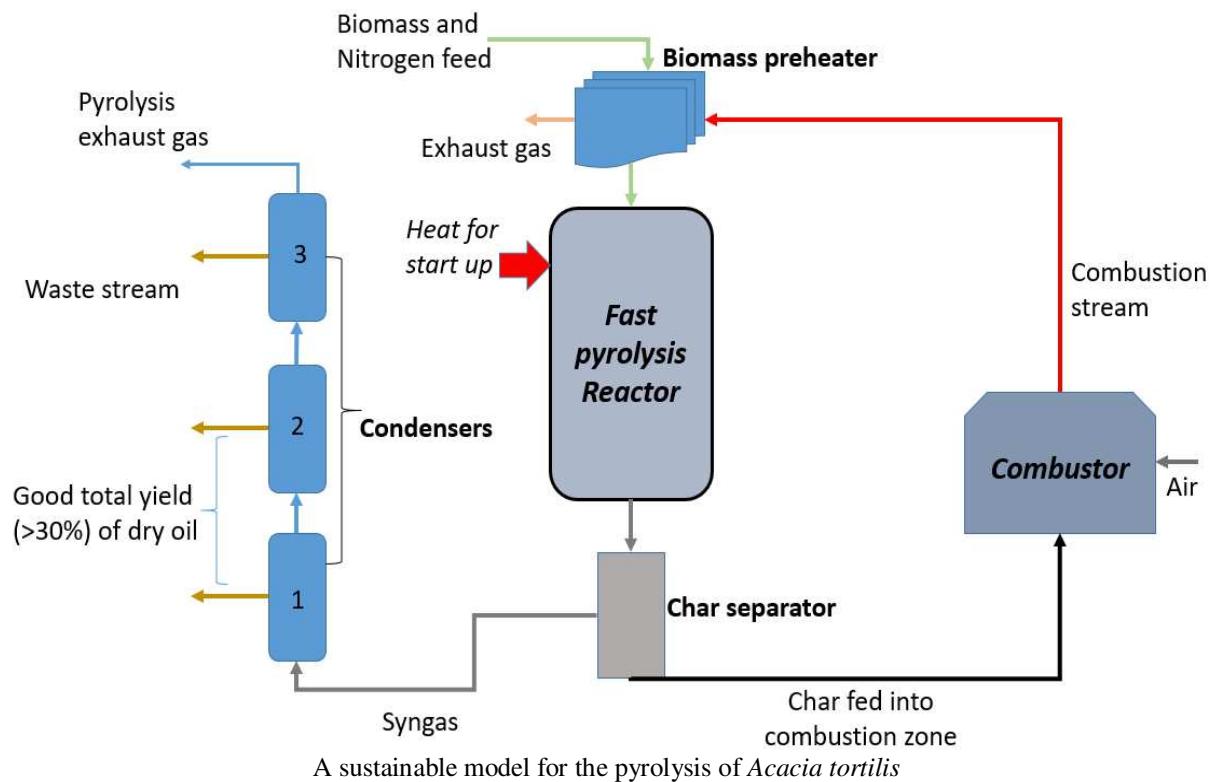
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A preliminary environmental analysis for a sustainable pyrolysis process of *Acacia tortilis* encroacher bush.

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Graphical Abstract



Abstract

A shortcut method of environmental assessment was applied procedurally to an *Acacia Tortillis* pyrolysis project which is in early stages of process development. The method uses mass balance data from the process simulation, which is done in ChemCAD. The ChemCAD model was developed using characterization data for raw biomass and the product bio-oil and data from literature. The shortcut assessment method started off by scoring the impact of inputs and outputs as high (A=1), medium (B= 0.3) and very low (C= 0) under impact categories such as raw material availability, use of critical materials, chronic toxicity, global warming potential, odour and eutrophication potential. An aggregated metric called the general effect index (GEI) was then calculated using this data and mass indices derived from mass balance. The GEI was calculated for inputs,

outputs and the overall process. It fell within the scale of 0-1, with values below 0.5 indicating a low environmental impact, while those above that threshold indicated high impact. A GEI of 0 for the inputs reflected on the renewability of biomass and neutral impact of nitrogen and air. A GEI of 0.370 for the outputs showed they do have a significant effect on the environment and organisms, though overall, the process is relatively benign. The impact could be further reduced by utilizing the fuel gas waste stream which has a high methane content. The results obtained generally tally with other literary findings on biomass pyrolysis.

Keywords

Bioenergy, environment, pinedust, pyrolysis, sustainability

Funding

There was no funding received to conduct this research.

Conflicts of interest/Competing interests

We declare that there is no conflict of interest or competing interests in this research.

Availability of data and material

Not applicable

Code availability (software application or custom code)

Not applicable

Authors' contributions

Gratitude Charis conceptualized the paper and simulation model. He also wrote the article. Edison Muzenda and Gwiranai Danha were involved in supervision, review and revision, including ensuring technical soundness and proper structuring of the article.

1. Introduction

Efforts of greening the brown economy have increased tremendously in the past two decades as ecological friendliness has been elevated as an equally important pillar of sustainability, along with technical and socio-economic aspects. Recent global and national policies have narrowed restrictions on emissions and some

process waste streams to curb their impact on the environment and on health. The most popular international policies on emissions emanated from the United Nations Framework Convention on Climate Change (UNFCCC) of 1994 and the follow up Kyoto protocol of 1997 which mainly addressed greenhouse gases and clean development strategies (UFCCC, 2003). These instruments set targets for various countries and regions to reduce the impact of anthropogenic emissions on climate change. Additionally, there have been many environmental restrictions and standards on waste compositions that could be toxic to any form of life, at international, regional or national levels. At industrial scale, emphasis is placed on process safety, which includes knowing the potential impact of any other process stream if it were to come in contact with human, and non-human life (Mannan et al., 2015). Such knowledge is vital in informing the safety policies and strategies that would be adopted for the facility. In view of these factors, it is important to be able to project the potential ecological impact of a process, beyond knowing its technical, economic and commercial viability. For such a targeted part of a Lifecycle Assesment (LCA), process simulation tools can be used to predict the potential environmental impact parallel to their use in assessing and enhancing the techno-economic feasibility of a production plant. This gate-to-gate, process-based Life Cycle Assessment (p-LCA) which focusses on one stage or a full process enables better process assessment and optimization with environmental impact in mind (Feng et al., 2018). For instance one can choose environmentally friendly inputs and process conditions that reduce waste products and also recycle or reuse some streams.

In this study, the environmental assessment of a pyrolysis process was carried out using a shortcut pLCA method described by Biwer & Heinze, (2004), which they recommended for early stages of process development when there is not yet much information on the process design. The method uses the mass balance from a ChemCAD simulation of the intended process to predict the environmental impact, using a set of defined standards. Conventionally, pLCAs are the most popular and accurate assessment methods that can be done flexibly for different definitions of system boundaries, especially within a process (Willskytt & Brambila-Macias, 2020). They usually require a detailed analysis of every impact source in the process, entailing a commitment of much time and resources. The shortcut pLCA method used in this case was designed to use as little information as available from a generic process flow sheet generated from a process simulation.

The objective was to obtain preliminary metrics that can be used to assess the environmental impact potential of the pyrolysis project and optimize the system to reduce waste. *Acacia tortilis*, an encroacher bush constantly thinned to replenish grazing lands in Botswana, was used as the pyrolysis feedstock. The overall metric used for

environmental assessment was the general effect index (GEI_{overall}), which is an average of the GEIs for the inputs and outputs. It is measured in the scale 0-1 and calculated as detailed in the report. Values below 0.5 imply that the overall process, inputs or outputs are relatively benign, while values over 0.5 generally imply that they are harmful to the environment. The values were subsequently compared to GEIs from other processes. All the percentage compositions referred to in this study are weight (wt) %.

2. Methodology

2.1 The ChemCAD model

The optimization of chemical processes often tackle economic and environmental objectives simultaneously through improved energy and resource efficiency, with reduced costs on waste management as well. The actual process flow sheet used in previously documented pyrolysis experiments (Figure 1) was deemed unsustainable due to the use of a fossil-based, high-cost energy source; the absence of energy integration or recovery and low yields of the targeted dry oil of high heating value (HHV) (Charis et al., 2020).

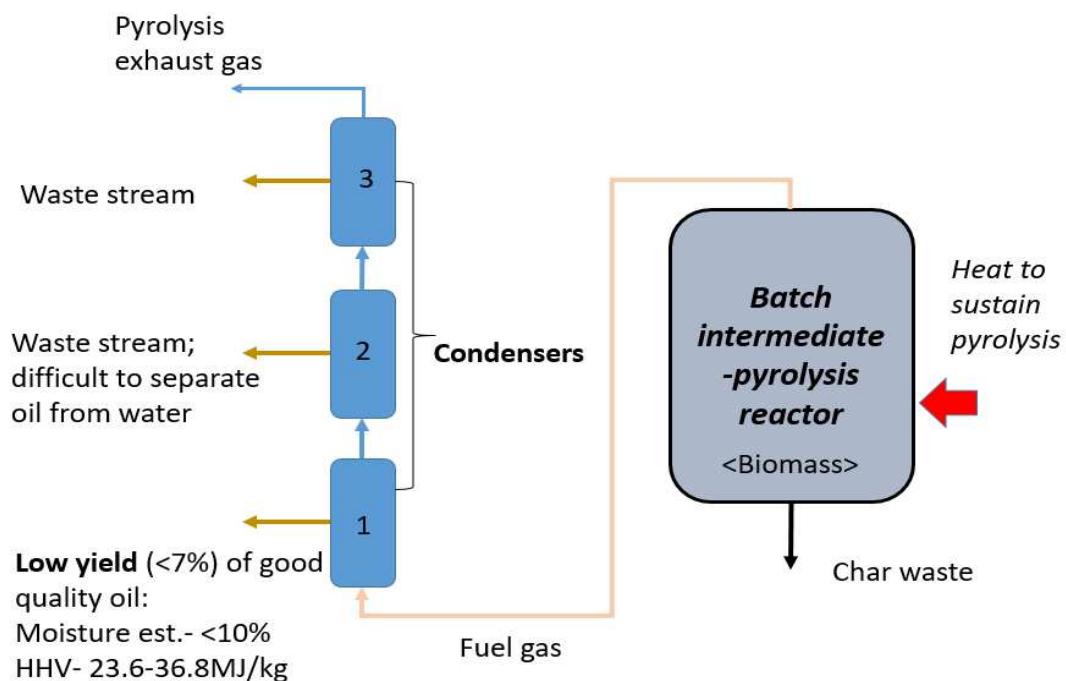


Figure 1. Pyrolysis flow diagram used in experiment

Figure 1 shows that two waste streams and one product stream were generated from the process. Furthermore, the use of fossil-based electricity as the source of energy makes the process more unsustainable. Figure 2 shows the conceptual model formulated to reduce waste streams, increase energy efficiency and reduce the overall environmental impact. The model involves the use of fast pyrolysis regime to improve overall quality of oil,

quantity of dry oil obtained in first two condensers and the recovery of energy from waste char (Gooty, 2012), (Bashir et al., 2017).

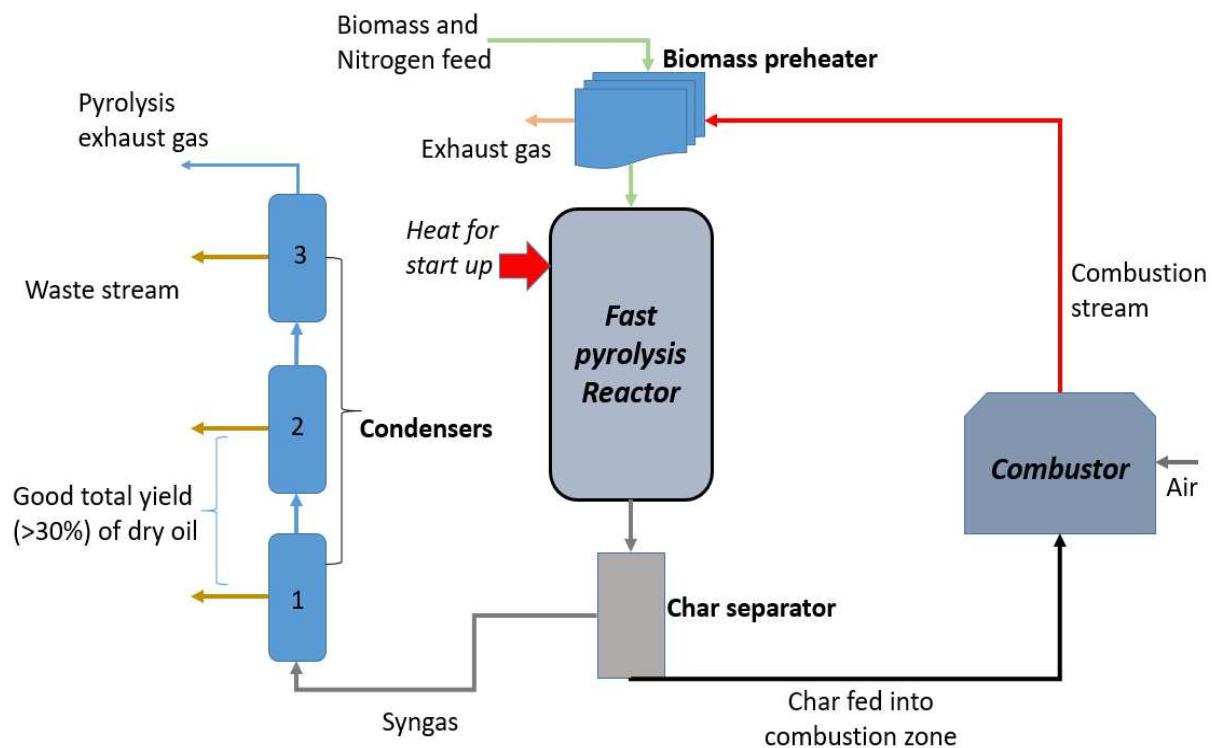


Figure 2. Flow diagram for a more sustainable pyrolysis model

A ChemCAD model was then constructed using the concept in Figure 2, by factoring in the yields of the bio-oil, char and fuel gas at the optimum pyrolysis temperature (500°C) using results from the experimental work. Optimization was done around the stage condensation units to obtain a maximum recovery of high quality oil (<10% moisture), which also results in a reduction of waste streams. The reaction yield method was preferred for this preliminary work because simulating biomass pyrolysis processes using kinetic models is very difficult and time consuming given the complex reactions and numerous components involved (Humbird et al., 2016), (Onarheim et al., 2015). The following detailed considerations were made in coming up with a complete flowsheet:

- **Bio-oil:** Bio-oil has over 100 compounds which cannot all be represented in the product model. The compositional analysis of the pine bio-oil using gas chromatography and a mass spectrometer (GCMS) indicated area composition of ~48% phenols and ~30% hydrocarbons the rest were carboxylic acids, ketones and sugars (Charis et al., 2020). Four compounds were chosen to represent bio-oil: two phenols with high peak areas (Cresol and Phenol, 4-ethyl-2-methoxy-), a medium-chained hydrocarbon

(Henecoisane) and a carboxylic acid (Benzoic acid). The total moisture content of water in the bio-oil is 26.4%, in agreement with literature which stipulates a value between 20% and 30% for fast pyrolysis oil (Oasmaa et al., 2012). In intermediate pyrolysis the amount of water can even go up to 50% and at such levels phase separation occurs. The total yield of bio-oil including water is 46.4%, which is just above the average total yield of 43% obtained by Charis et al. (Charis et al., 2020) at 550°C to reflect fast pyrolysis conditions.

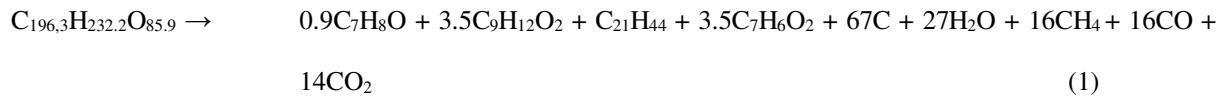
- **Char:** The char was assumed to be pure carbon to keep the model simple. This is good approximate since char is a result of removal of impurities leaving an almost pure carbon residue. The yield of char was taken as 20.3%.
- **Fuel gas:** The non-condensable gases were modelled as containing methane, carbon monoxide, carbon dioxide and hydrogen which are major constituents in the actual pyrolysis operations. The total yield of this gas was taken as 33.3%, which is within the range obtained in the experiments (Charis et al., 2019).

A brute formula for the biomass was derived using the above considerations, ultimate analysis results, literature and stoichiometric balance of the pyrolysis reaction (Table 1).

Table 1: Determination of pinedust empirical and brute molecular formula for the simulation. (Nitrogen and sulphur are excluded)

Basis- 100g of biomass	Acacia Holosericea	Acacia trunk	Cincinatta	Acacia Tortilis	General biomass model, formula C ₁₀₀ H ₁₂₀ O ₄₀ (Freda et al., 2011)
C	44.03	46.44	41.57	-	
H	5.67	5.98	5.15	-	
O	50.05	44.45	52.15	-	
N	0.25	0.23	0.25	-	
S	Not detected	Not detected	Not detected	-	
Mole ratio and C based Empirical formulae	C _{3.87} H _{5.98} O _{3.13} CH _{1.55} O _{0.85}	C _{3.87} H _{5.98} O _{2.78} CH _{1.55} O _{0.72}	C _{3.45} H _{5.11} O _{3.26} CH _{1.48} O _{0.94}	C ₅ H ₆ O ₂ CH _{1.20} O _{0.40}	
The formula adopted for simulation	Mole ration based: C _{4.95} H _{5.90} O _{2.17} C-based empirical: CH _{1.19} O _{0.43} Molecular: C _{196.3} H _{232.2} O _{85.9}				

The balanced stoichiometric equation that takes into account the yields discussed earlier would be in the form:



The next step was then to build the representative process simulation model and optimize it for low waste and high efficiency. The stoichiometric reactions were modelled in an equilibrium reactor, specifying a 100% conversion of *Acacia tortilis* and a 15% conversion of methane. The stoichiometric block was used to represent the char combustor, while flash units were used for the condensers. A heat exchanger was used for the preheater and a general separator to divert at least 95% of the char to the combustor. The gases go to the staged condensation line where the condensable bio-oil and water are recovered. The condensation temperatures were to be optimized such that oil with water content below 10% would be recovered in the first two condensers while a waste product comprising mostly water and acid, was recovered from the third condenser. The remaining gas, which is mostly non-condensable can be fed into the combustor or vented out.

2.2 Optimization of the process

The condensation system was optimized to maximize the recovery of a high quality bio-oil product with <10% moisture, while reducing the liquid waste from the process. The waste was reduced by separating the water from the oil to avoid a stream with a considerable amount of oil mixed with waste, which cannot be distilled at conventional heating rates without decomposing, therefore is discarded as waste (Charis et al., 2020).

The first step was to find the primary condenser temperature giving a high total flow rate of oil of acceptable quality a of oil, with 3-10% water content. A sensitivity analysis was run for the primary condenser temperature in the range 80°C to 120°C to find that optimum point or range. The aim was to obtain a good trade-off between high oil yield (flowrate) and good quality of oil, denoted by low water composition and consequently, a high HHV. A secondary indicator of the bio-oil quality is a low acid composition (higher pH) otherwise, the bio-oil would be corrosive.

When the optimum point was established for the primary condenser, it was fixed while the secondary condenser was varied from 60-100°C to find the point at which the remaining high quality oil could be further recovered.

We carried out a separate sensitivity study to determine how the stream yield and composition from the secondary condenser would respond to a variation of the primary condenser temperature from 80°C to 120°C.

2.3 The shortcut environmental assessment (SEA) process

2.3.1 Description of the procedure

We then carried out the SEA method using the mass balances from the optimized process flowsheet. First of all, we classified inputs and outputs into impact categories (ICs) and impact groups (IGs) using the procedure outlined in Figure 3. These gave values according to the ABC classification, which were then used to obtain environmental factors (EF). EF_{Mw} selected for this study, in particular, uses A=1 for high, B=0.3 for medium and C=0 for zero impact materials. For instance, under the IC number 4 of thermal risks, a material of high flammability would be classified as A while a less flammable one would be a B and a non-flammable or fire resistant material would be a class C.

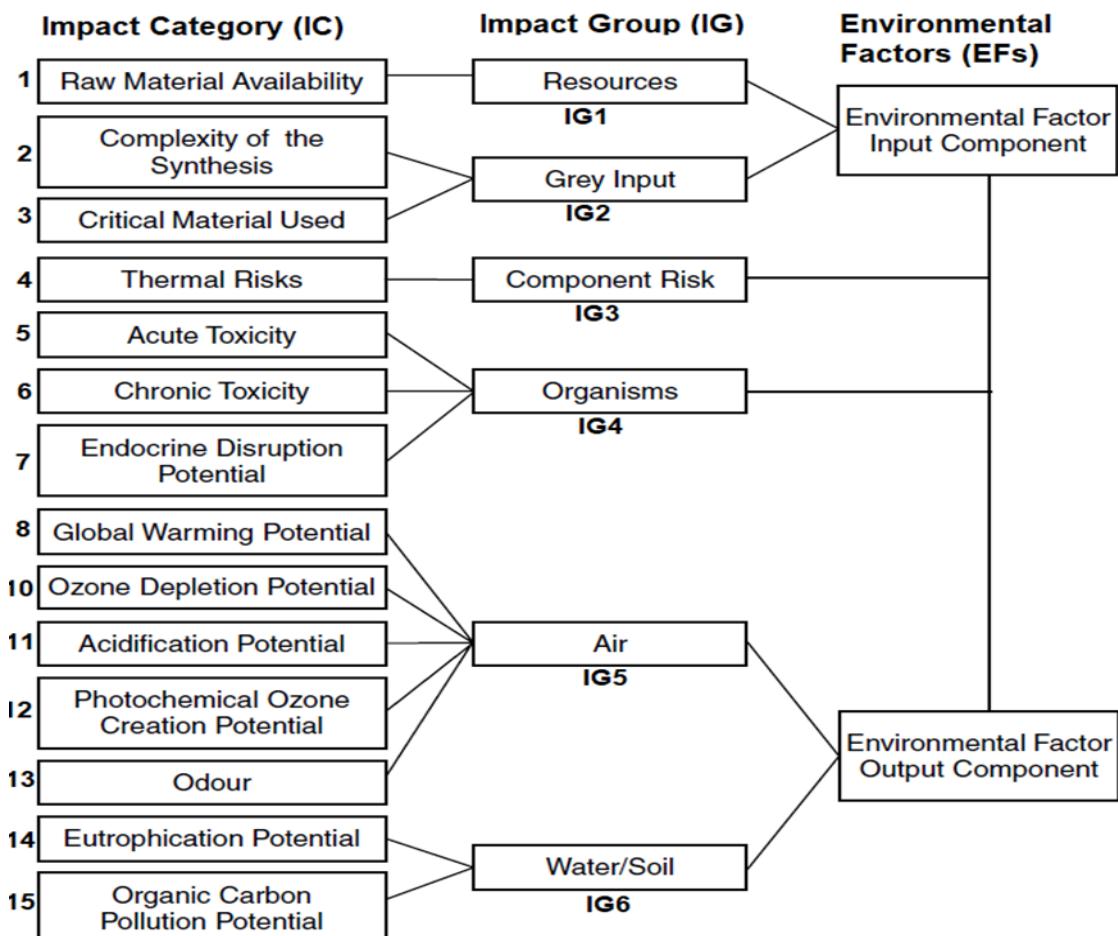


Figure 3. Impact categories, groups and environmental factors. Adapted from Biwer & Heinze, (2004)

From Figure 3, IG_1 and IG_2 are only relevant to the inputs; IG_3 and IG_4 to both inputs and outputs, while IG_5 and IG_6 apply to outputs only. The rest of the terms used are defined by the following expressions, where i refers to input components and j refers to the outputs:

- Environmental factors, EF_i and EF_j

$$EF_i = \frac{IG_{1,i} + IG_{2,i} + IG_{3,i} + IG_{4,i}}{i} \quad (4)$$

$$EF_j = \frac{IG_{3,j} + IG_{4,j} + IG_{5,j} + IG_{6,j}}{j} \quad (5)$$

For expressions 4 and 5 the IG value is taken as the maximum value of the ICs in that group. For instance, if there is an A, B and a C in IG_4 for an input component 1, $IG_{4,1} = 1$.

- The Mass Index (MI) of an output component j is given by:

$$MI_j = \frac{m_j}{m_p} \quad (6)$$

Where m_j is mass of the component, and m_p is the mass of the desired product.

The EFs were added together to give environmental indices, which were aggregated with mass indices (MIs) for the process, calculated using the mass balance (see Figure 4).

- The environmental index (EI) was then obtained as follows:

$$EI_j = \frac{EF_j \times m_j}{m_p} = EF_j \times MI_j \quad (7)$$

- The Environmental Index (EI) of the process as EI_{IN} or EI_{OUT} were obtained from:

$$EI_{IN} = \sum_{i=1}^{IN} EI_i \quad (8)$$

OR

$$EI_{OUT} = \sum_{j=1}^{OUT} EI_j \quad (9)$$

- The general effect index (GEI) of the process were given by:

$$GEI_{INPUTS} = \frac{EI_{IN}}{\sum MI_i} \quad (10)$$

$$GEI_{OUTPUTS} = \frac{EI_{OUT}}{\sum MI_j} \quad (11)$$

Using the calculations above, the GEI values would fall in a range between 0 and 1. A GEI lower than 0.5 indicated low impact inputs or products. The overall GEI would then be an average of the GEI_{INPUTS} and $GEI_{OUTPUTS}$. The procedure followed is summarized in Figure 4, where obtaining the $GEIs$ for the process is the objective.

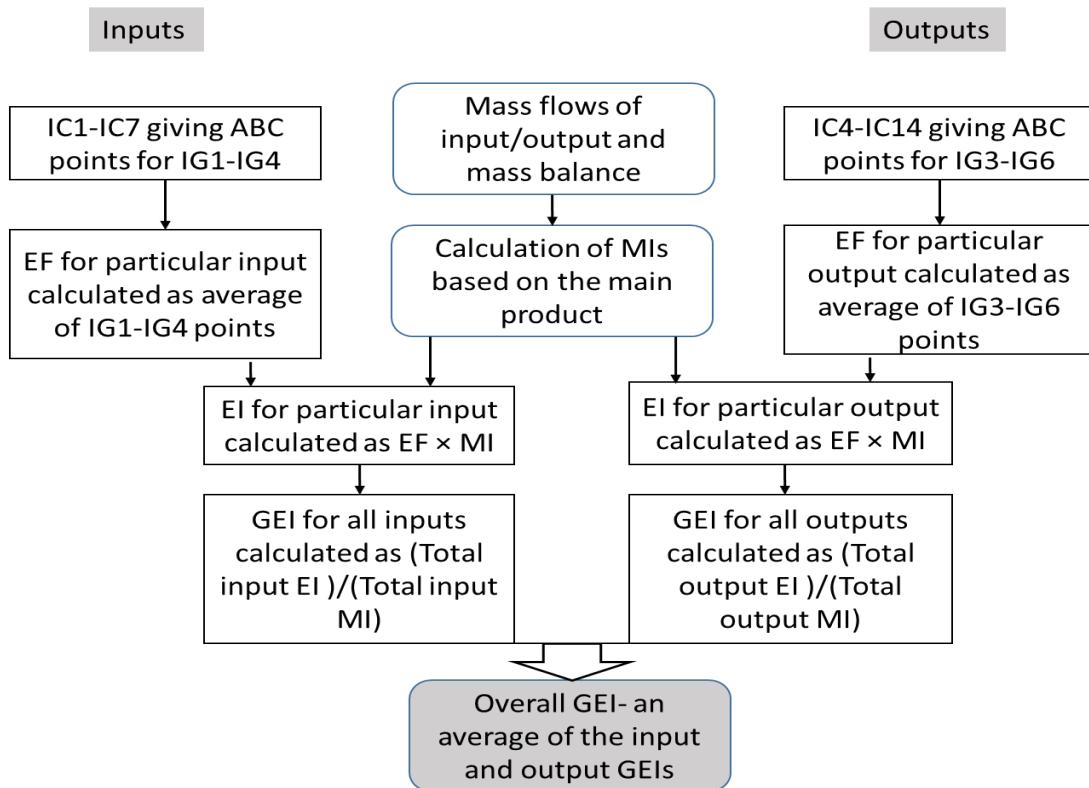


Figure 4. The assessment process summarized

2.3.2 Determining the right ICs for input and output components

Three inputs were considered: *Acacia tortilis*, nitrogen for the inert atmosphere and air that is used in the char combustor. The biomass is a renewable resource with no critical compounds, low thermal risk, no chronic or acute toxicity and no hormonal effects known. This explains why the category C was assigned for IC1, IC4, IC5, IC6 and IC7. The pyrolysis synthesis stage is also less than 3 stages, requiring no critical materials; this explains why IC2 and IC3 were also assigned C=0. The air and nitrogen also qualified for category C for IC1-IC7.

For the products, only the dry bio-oils and syngas were deemed to have a moderate thermal risk due to their relatively high combustibility. The liquid products were deemed moderately toxic due to the presence of a wide

range of organics, including acids; which could exhibit acute or chronic toxicity when ingested. The carcinogenic effects of wood pyrolysis vapours is two to three times less than coal fumes (NREL, 1997). Nonetheless, the vapours are malodorous and contain carbon monoxide and toxic organics including some four and five-ring polycyclic aromatic hydrocarbons (PAHs) that can lead to other chronic lung infections. In view of the points mentioned, the product and waste streams were classified as at least moderately harmful to organisms. The liquid product and waste streams were considered harmless to the air. The pyrolysis and combustion exhaust gases have significant amounts of carbon dioxide and methane which are greenhouse gases with moderate to high ABC impact points in the ICs under the air IG. Both gaseous exhaust products were considered to have a high global warming potential due to the presence of either methane or carbon dioxide, assuming they are both vented into the atmosphere. The pyrolysis exhaust gas could be further separated using a membrane or carbon dioxide absorbents, to give a methane-rich product. Such a fuel gas can be introduced directly in the combustor or used in an integrated gas combined cycle (IGCC) engine to generate heat for drying biomass or other purposes. Most of the liquid products have several organic carbon compounds that preferentially dissolved in either the aqueous or oil phases, giving them a moderate organic carbon polluting potential.

Definition of terms used in Table 2

ThOD: Theoretical Oxygen Demand

COD: Chemical Oxygen Demand

E: European Union classification.

R: R-codes

CH-poison class: Swiss poison classes

ERPG: Emergency Response Planning Guidelines (American Hygiene Association)

IDLH: Immediately Dangerous to Life and Health (National Institute for Occupational Health and Safety)

LC, LD: Lethal Concentration/Dose

MAK: German workplace threshold value (Maximale Arbeitsplatzkonzentration)

IARC: classification of International Agency for Research on Cancer

Unit Risk: cancer risk, according to the United States (US) Environmental Protection Agency)

NFPA: hazard classes US National Fire Protection Agency (H- Health, F- Flammability, R- Reactivity); fp- flash point; ait- auto ignition temperature; T decomp- decomposition temperature;

$\log(\lambda)$: logarithm of electric conductivity

WGK: German water hazard classes (Wassergefährdungsklassen)

I, I/O, O: Input (only), Input/Output, Output (only)

Table 2: Criteria for classifying ICs. Adapted from (Biwer & Heinze, 2004).

Impact category	Class A	Class B	Class C
Raw Material Availability (I)	Only fossils, predicted exhaustion in 30 years	Only fossils, predicted exhaustion in 30–100 years	Renewable/long term supply (>100 years)
Complexity of the Synthesis (I)	>10 stages	3–10 stages	<3 stages
Critical Materials Used (I)	Critical materials like heavy metals, AOX, PCB used-produced in stoichiometric amounts	Critical materials involved in sub-stoichiometric amounts, stoichiometric amounts of undesirable material	No critical compounds involved
Thermal Risk (I/O)	1. R 1, 3, 4, 9, 12, 15–17, 30; EU: F+, E; NFPA F + R: 3, 4 2. fp <38 °C; ait <38 °C; T decomp <38 °C; $\log(\lambda) = -12$ to -11 ; unstable groups: nitro, ether, peroxy	1. R 2, 5–8, 10, 11, 14, 18, 19, 30, 44; EU: F, O; NFPA F + R: 2 2. 38 °C < fp <100 °C; 38 °C < ait <100 °C; 38 °C < T decomp < 100 °C; $\log(\lambda) = -10$ to -8 ; unstable: azo, cyanate	1. NFPA F + R: 0, 1 2. fp > 100 °C; ait >100 °C; T decomp > 100 °C; $\log(\lambda) > -8$; no unstable groups
Acute Toxicity (I/O)	1. EU: T+ ; R 26–28, 32, 50; CH-poison class: 1, 2; NFPA H: 4; WGK 3 2. ERPG: <100mgm; IDLH: <100mgm ⁻³ 3. LC ₅₀ inh <200mg m ⁻³ ; LD ₅₀ oral <25mgkg ⁻¹ ; LC ₅₀ der <50mgkg ⁻¹	1. EU: T, Xn, Xi, C; R 20–25, 29, 31, 34–39, 41–43, 51, 52, 54–57, 65; CH-poison class: 3, 4; NFPA H: 2, 3; WGK 2 2. ERPG: 100–1000mgm ⁻³ ; IDLH: 100–1000mg m ⁻³ 3. LC ₅₀ inh 200–2000mgm ⁻³ ; LD ₅₀ oral 25–200mg kg ⁻¹ ; LC ₅₀ der 50–400mgkg ⁻¹	1. CH-poison class: 5; NFPA H: 0, 1; WGK 1 2. ERPG: >1000mgm ⁻³ ; IDLH: >1000mgm ⁻³ 3. LC ₅₀ inh 2000mgm ⁻³ ; LD ₅₀ oral >200mgkg ⁻¹ ; LC ₅₀ der >400mgkg ⁻¹
Chronic Toxicity (I/O)	1. MAK: <1mgm ⁻³ ; IARC: 1, 2A; R 45–49, 60, 61, 64 2. Unit risk: 10 ⁻⁴ –10 ⁻⁵	1. MAK: 1–10mgm ⁻³ ; IARC: 2B, 3; R 33, 40, 53, 58, 62, 63 2. Unit risk: 10 ⁻⁶ –10 ⁻⁸ 3. EU: T, T+, Xn; CH-poison class: 1, 2	1. MAK: >10mgm ⁻³ ; IARC: 4 2. Unit risk: >10 ⁻⁹ 3. CH-poison class: 3, 4, 5
Endocrine Disruption Potential (I/O)	–	Scientifically proved/suspicion	No hormonal effect is known
Global Warming Potential (O)	Global Warming Potential (GWP) > 20	GWP < 20	No global warming potential
Ozone Depletion Potential (O)	Ozone Depletion Potential (ODP) > 0.5	ODP < 0.5	No ozone depletion potential
Acidification Potential (O)	Acidification Potential (AP) > 0.5	AP < 0.5	No acidification potential
Photochemical Ozone Creation Potential (O)	Photochemical Ozone Creation Potential (POCP) > 30 or NO _x	30 > POCP > 2	POCP < 2 or no effect known
Odour (O)	–	Odour <300mgm ⁻³	Odour >300mgm ⁻³
Eutrophication Potential (O)	N-content > 0.2 or P-content > 0.05	N-content < 0.2 and P-content < 0.05	Compound without N and P
14. Organic Carbon Pollution Potential (O)	–	ThOD and COD >0.2 g O ₂ g ⁻¹ substrate	ThOD and COD < 0.2g; O ₂ g ⁻¹ or no organic compound

3. Results and discussion

3.1 The optimized process flowsheet

The flowsheet is optimized for a maximum recovery of dry oil, which is better done using the first two condensation stages rather than the first one alone. The sensitivity analysis on the first condenser produced the trend shown in Figure 5.

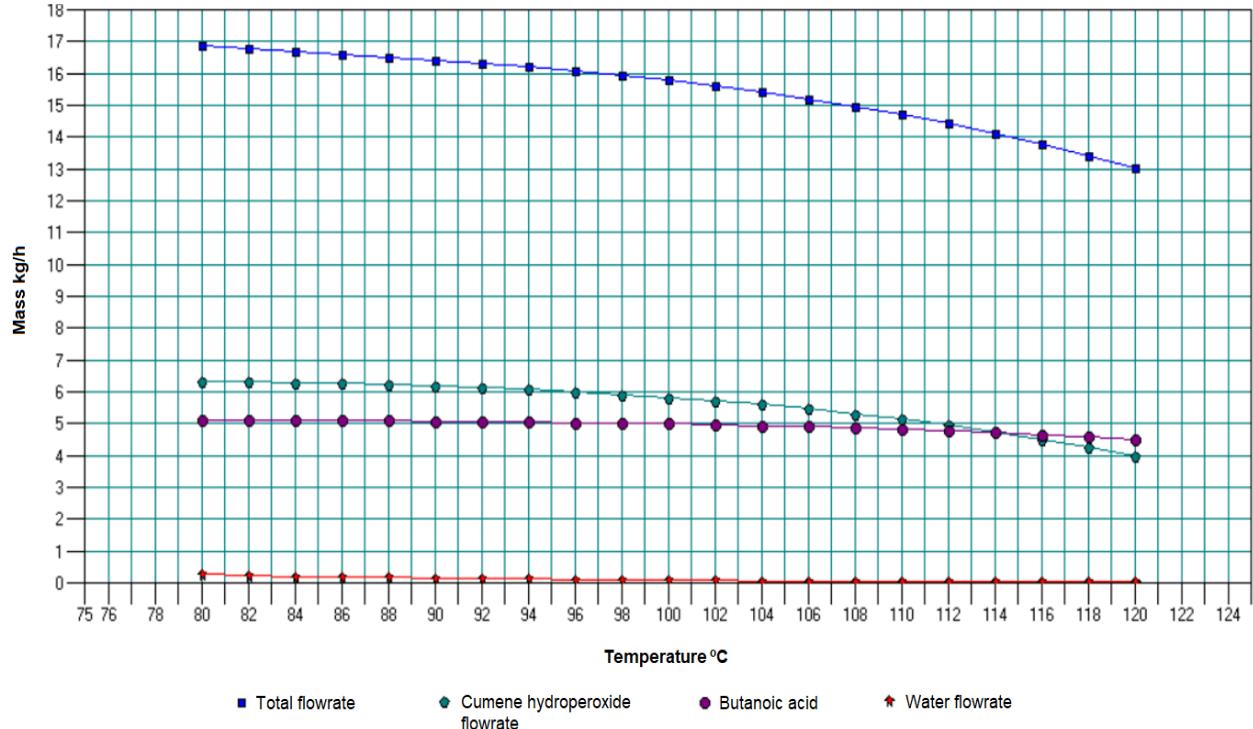


Figure 5. Sensitivity analysis for the first (primary) condenser

Figure 5 shows that at lower temperatures such as 80°C, it is possible to obtain a good quantity (up to 16.9kg/h) of dry oil with just below 2% moisture content (MC). At this temperature however, the rest of the streams obtained from stage 2 and stage 3 condensers are both wastes with MCs of at least 50%. Using intermediate temperatures such as 96°C on the primary condenser brings about a separation regime that is not sharp and decisive. For instance, combining with 78°C on second condenser gives an overall productivity of 16.6kg/h dry oil for both condensers, but the the second condenser dry oil has MC >10%. At higher second condenser temperatures above 82°C, we can achieve MCs below 5%, however with a low overall productivity/yield (<16.5kg/h) at both condensers.

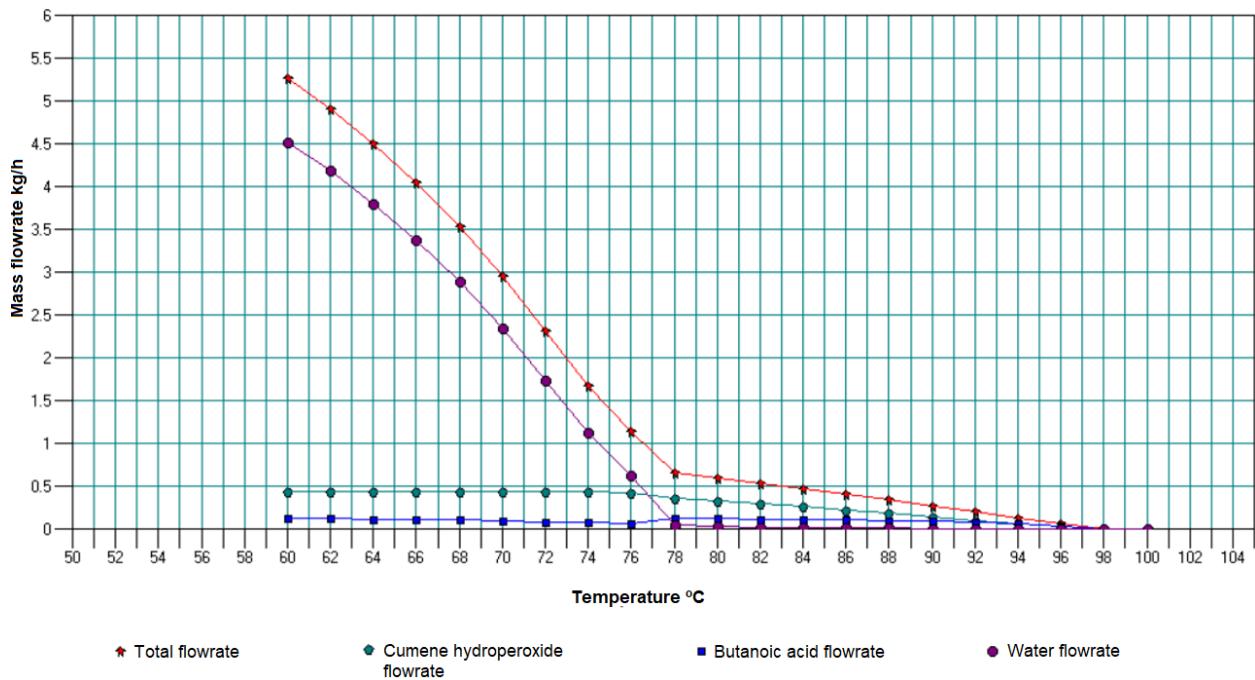


Figure 6. Sensitivity analysis for the secondary condenser, at 96°C primary condenser temperature

At higher primary condenser temperatures above 105°C, there are sharper separations in the secondary condenser with meaningful overall yields of the dry-oil of less than 10% MC. For instance, at 114°C primary condenser temperature, 14kg/h of dry oil (<1%MC) is recovered in the primary condenser, while 2.8kg/h of dry oil (<7%MC) is recovered subsequently, in the secondary condenser at 78°C. This makes it possible to recover a total of 16.8kg/h dry oil, which is a yield of 33.6%. The primary and secondary condenser of temperatures of 114°C and 78°C respectively are adopted for this simulation.

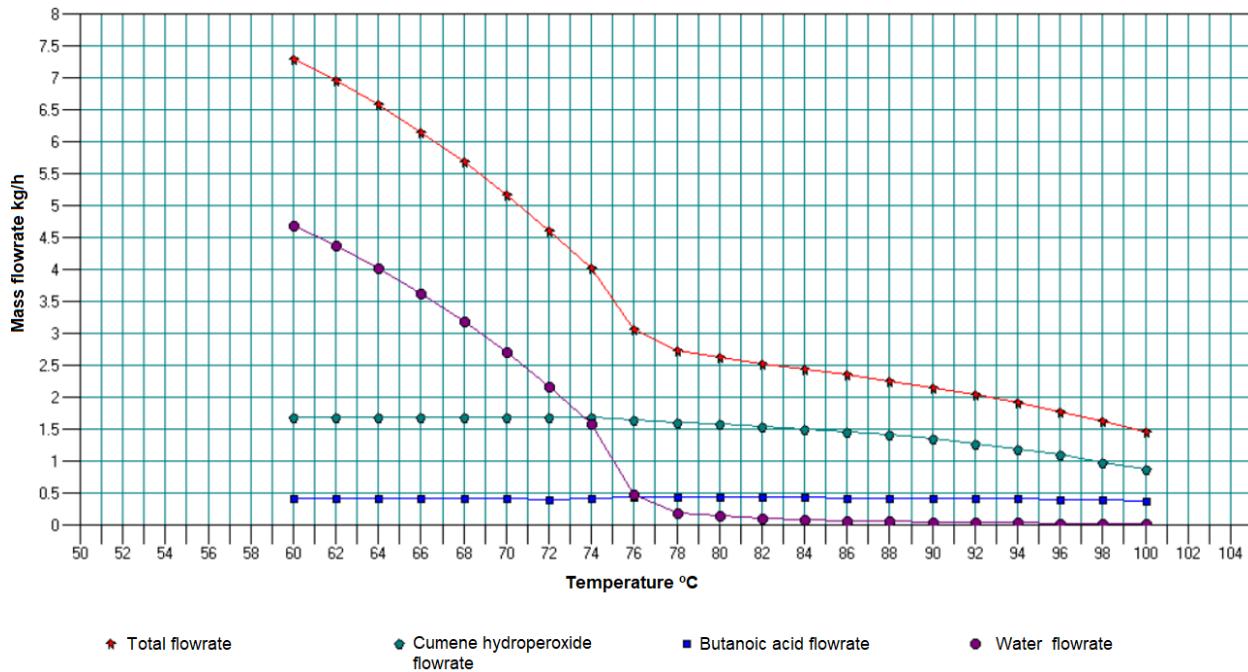


Figure 7. Sensitivity analysis for the secondary condenser at 114°C primary condenser temperature.

A quick survey of other literature results for the pyrolysis of various biomasses was done to validate the simulation results.

Table 3: Comparison of simulation results to literary cases of staged fraction condensations

Biomass and reactor		Temp of condenser: outlet vapor	MC /wt%	Total yield/ wt%	HHV of product/ MJ/kg
Birch bark pyrolysis in bubble fluidized bed reactor (Gooty, 2012)	<i>First condenser oil</i>	105 °C	< 1%	35%	31 MJ/kg
	<i>Second condenser dry oil</i>	-	-	-	-
	<i>Aqueous waste</i>	< 15 °C	60%	20%	-
Red oak pyrolysis in fluidized bed reactor (Pollard et al., 2012)	<i>First condenser oil</i>	102°C	6.6%	21%	24.2-24.8 MJ/kg
	<i>Second condenser dry oil</i>	77°C	9%	5.5%	-
	<i>Aqueous waste</i>	18°C	63.3%	21%	-
Pinewood pyrolysis in fluidized bed reactor (Papari & Hawboldt, 2018)	<i>First condenser oil</i>	115°C	2.5%	20%	24 MJ/kg
	<i>Second condenser dry oil</i>	-	-	-	-
	<i>Aqueous waste</i>	Coolant at 20°C	-	-	-
Kraft lignin	<i>First condenser oil</i>	105 °C	< 1%	25%	31 MJ/kg

pyrolysis in bubble fluidized bed reactor (Gooty, 2012)	<i>Second condenser dry oil</i>	-	-	-	-
	<i>Aqueous waste</i>	< 15°C	90%	13%	-
	<i>First condenser oil</i>	114°C	<0.7%	~28%	-
	<i>Second condenser dry oil</i>	78°C	7%	5.6%	-
<i>Aqueous waste</i>	~25°C	95.7%	14.2%	-	

The literature results show very low moisture contents for primary condenser temperatures above 105°C. For instance for Birch bark and Kraft lignin pyrolysis, which both had dry oils with <1% MC and yields of 35% and 25% respectively. The red oak pyrolysis also had similar results with our simulation on the secondary condenser, with a temperature of 77°C and MC of 9%, while this work had 78% and 7% respectively. The primary condensers in the shown literature used temperatures in the range 102-115°C, obtaining dry oil with <1 wt% to 6 wt% water.

3.2 Results of the SEA

From the mass balance using the flowsheet with primary and secondary condenser temperatures at 114°C and 78°C respectively, we obtained the metrics outlined in Table 3, extracted from Excel.

Table 3. Environmental assessment for early process development of Acacia pyrolysis

1. Inputs		Quantity, (kg/h)	MI	IC1	IC2	IC3	IC4	IC5	IC6	IC7	IC8	IC9	IC10	IC11	IC12	IC13	IC14	IG1	IG2	IG3	IG4	EF	EI
1 Raw material 1 (Biomass)	50	3,54	C	C	C	C	C	C	C									0	0	0	0	0	0,000
2 Raw material 2 (Air)	6	0,42	C	C	C	C	C	C	C									0	0	0	0	0	0,000
3 Raw material 3 (Nitrogen)	0,003	0,00	C	C	C	C	C	C	C									0	0	0	0	0	0,000
Total	56,003	3,97																			GEI_inputs:	0,000	
2. Outputs		MI	IC1	IC2	IC3	IC4	IC5	IC6	IC7	IC8	IC9	IC10	IC11	IC12	IC13	IC14	IG3	IG4	IG5	IG6	EF	EI	
1 Dry bio-oil 1	14,12184	1,00				B	B	B	C	C	C	C	C	B	C	B	0,3	0,3	0,3	0,3	0,3	0,300	
2 Dry bio-oil 2	2,72	0,19				B	B	B	C	C	C	C	C	B	C	B	0,3	0,3	0,3	0,3	0,3	0,058	
3 Aqueous waste	7,1144	0,50				C	C	B	C	C	C	C	C	C	C	B	0	0,3	0	0,3	0,15	0,076	
4 Pyrolysis Exhaust gas	16,8034	1,19				B	B	A	C	A	C	B	C	C	C	C	0,3	1	1	0	0,575	0,684	
5 Combustion Exhaust gas	15,243	1,08				C	B	B	C	A	C	C	C	C	C	C	0	0,3	1	0	0,325	0,351	
Total	56,00264	3,97																		GEI_outputs:	0,370		
			- IG Resources	- IG Grey Input	- IG Component Risk	- IG Organisms		- IG Air			- IG Water/Soil										GEI overall	0,18513	

The inputs had a GEI of 0, implying that they generally have no negative impact on the environment and health of organisms. The outputs do have a notable impact, however, the GEI (0.370) is below 0.5 showing that it is still minimal in comparison with other processes. The overall process GEI ($GEI_{OVERALL}$) is 0.185.

Case studies of SEAs presented by Biwer and Heinze (Biwer & Heinze, 2004) confirmed that using greener bio-processes can drastically reduce the environmental impact compared to traditional chemical processes. For instance, the traditional process of producing 6-aminopenicillac acid from penicillin G using a traditional process scored an GEI_{INPUTS} of ~0.354 compared to the enzymatic process with GEI_{INPUTS} ~0.01. The traditional process inputs were based on oil and natural gas, which caused higher IG_1 (Resources) and IG_2 (Gray inputs) ratings. It also had toxic inputs such as butanol, phosphorous pentachloride and dichloromethane which resulted in a high IG_4 (Organisms) rating. Both GEIs for the inputs are higher than the pyrolysis process showing that it is relatively environmentally benign. Biwer and Heinze also discussed alternative routes for the fermentative production of pyruvate, which had $GEI_{OVERALL}$ values of 0.07, 0.115, 0.145 and 0.235 depending on the solvent/chemicals used as required by the separation process route.

Though the pyrolysis $GEI_{OVERALL}$ (0.185) is commendably lower than other processes, it is on the higher end for green processes, due to the presence of compounds that have potential chronic toxicity effects on organisms and greenhouse effects on the air. The pyrolysis syngas and oil contain some carcinogenic components such as polycyclic aromatic hydrocarbons (PAHs). To enhance process safety, the mechanical design of pipes and vessels should be air-tight to ensure that there are no leaks of the pyrolysis vapours. The syngas can be further purified by capturing carbon dioxide to remain with a methane-rich fuel gas which can be combusted in an IGCC engine for energy. The aqueous waste can be neutralized and disposed at different, non-arable sites to avoid much organic carbon loading. This waste is a much less severe problem compared to underground contamination by heavy metals, for instance.

4. Conclusion

In the early stages of process design, it is important to be able to predict the economic performance of a project and its environmental impact using the little information available at that point. The pyrolysis process was simulated in ChemCAD using a careful selection of representative compounds that approximate the physico-chemical properties

of the bio-oil, char and gaseous products. For the optimized flowsheet, temperatures of 114°C and 78°C were selected for the primary and secondary condensers respectively. It was concluded that these conditions or those in the vicinity gave the best opportunity for both a high quantity and quality of dry oil product, while reducing the number of waste streams to be managed. The ChemCAD model also produced results that concur with literature on staged condensations in biomass pyrolysis, therefore its mass balance was considered to be a good input for the SEA. The SEA method based on process simulation results enabled the evaluation of environmental effects at such early stages in a cost-effective and time-efficient manner. The GEI_{INPUTS} of 0 reflected the fact that the feedstock used is renewable and that the air, biomass and nitrogen have a negligible impact on the health of organisms and the environment. The GEI_{OUTPUTS} of 0.370 for the outputs, below the 0.5 threshold, showed that they are relatively benign to the environment and organisms. The GEI_{OVERALL} was lower at 0.185, which is a very good value in comparison to fossil-derived processes, though on the higher end for green processes. The environmental impact could be lowered further if the syngas is combusted before or after separating carbon dioxide, to reduce the amount of methane released to the atmosphere. Methane is a high impact GHG gas. The shortcut method was applied successfully using the mass balance and the representative compounds, yielding expected results.

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Figures

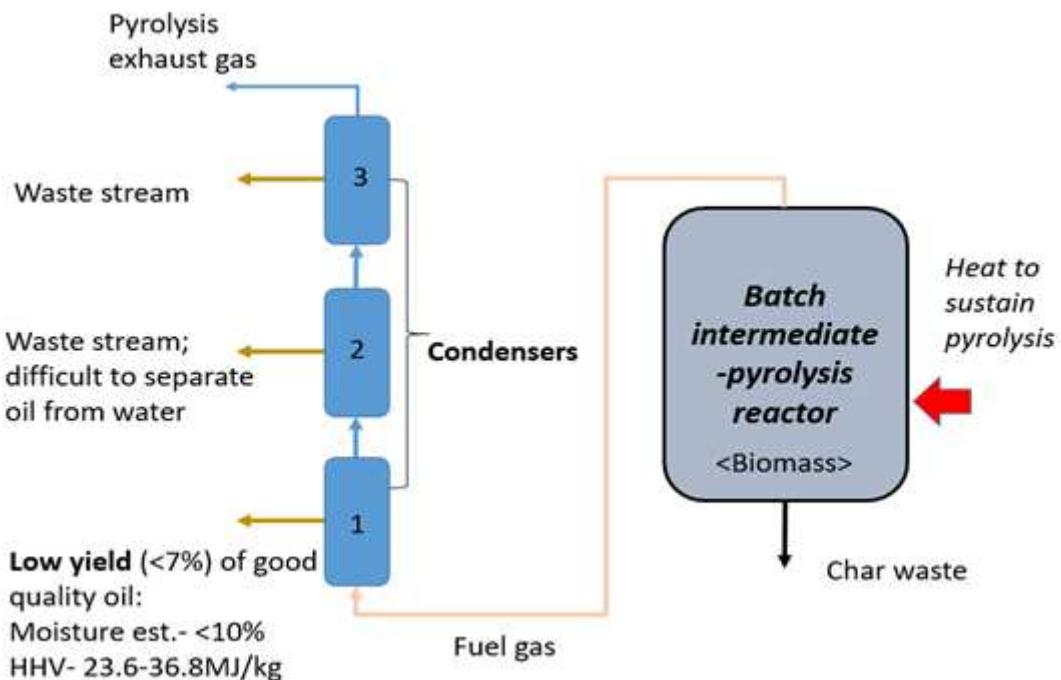


Figure 1

Pyrolysis flow diagram used in experiment

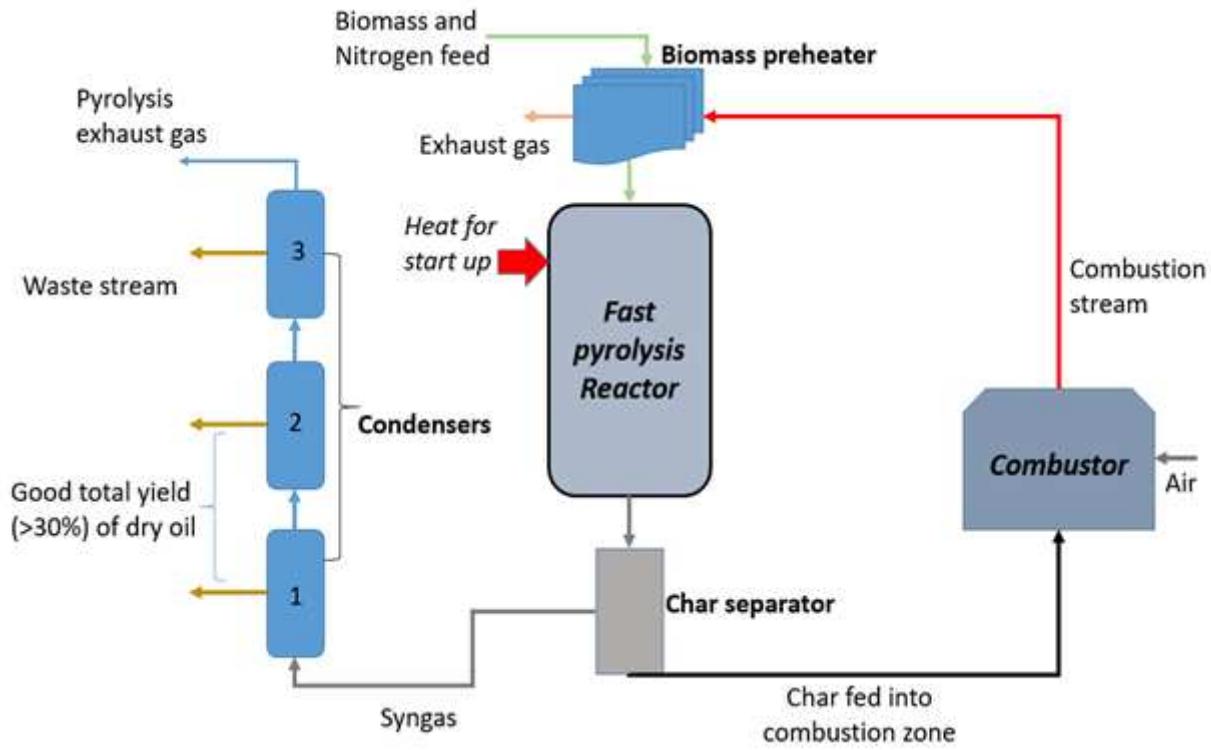


Figure 2

Flow diagram for a more sustainable pyrolysis model

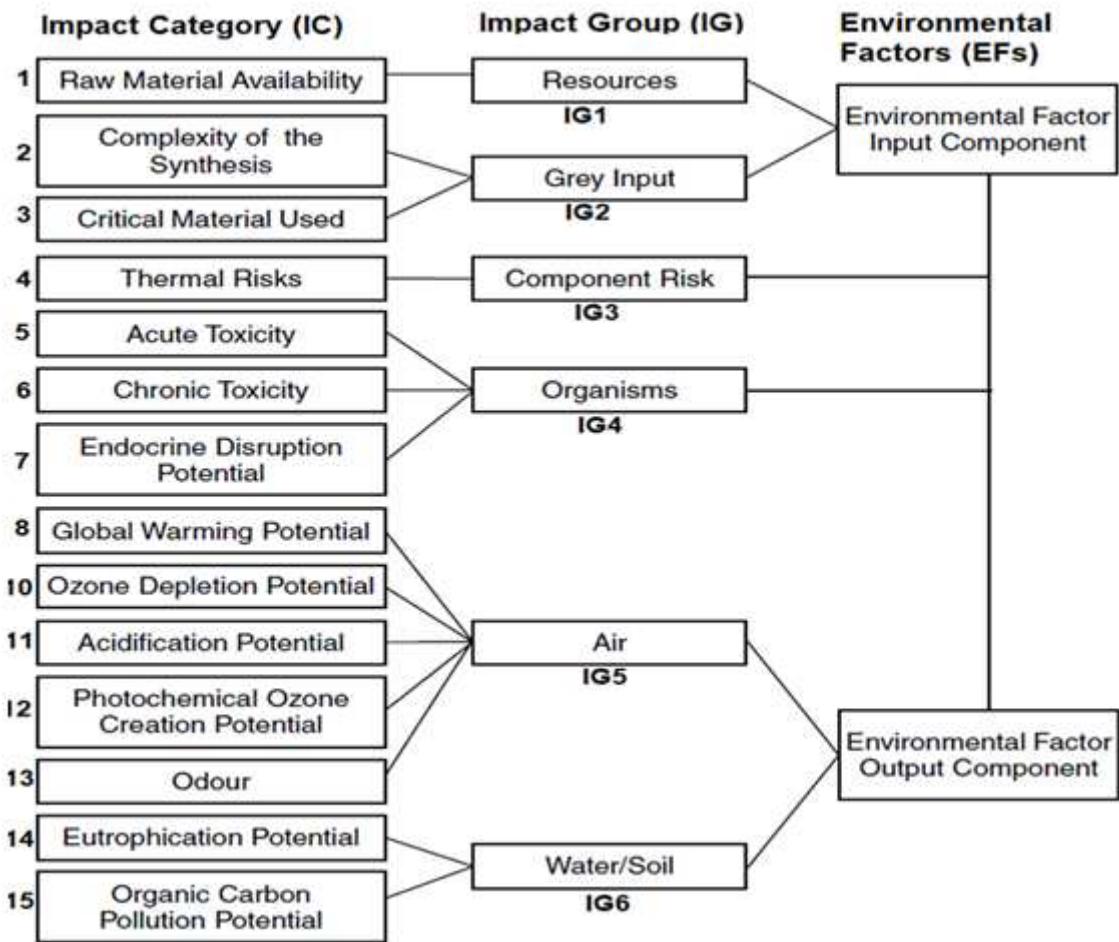


Figure 3

Impact categories, groups and environmental factors. Adapted from Biwer & Heinze, (2004)

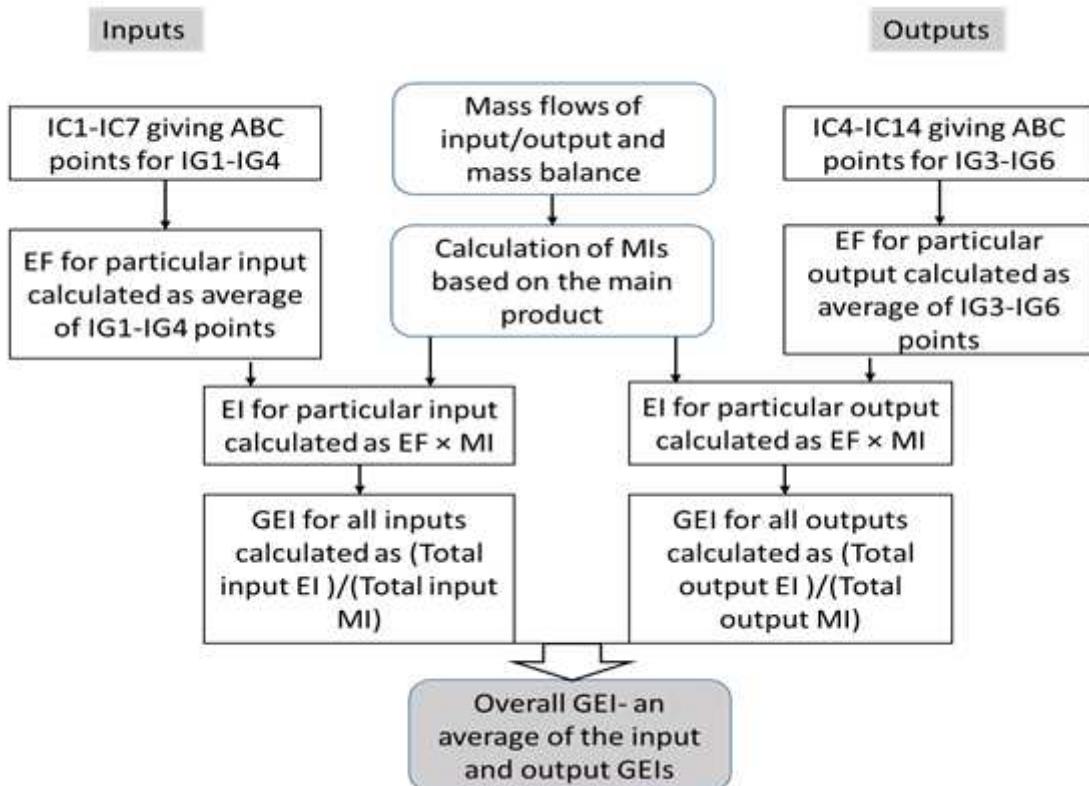


Figure 4

The assessment process summarized

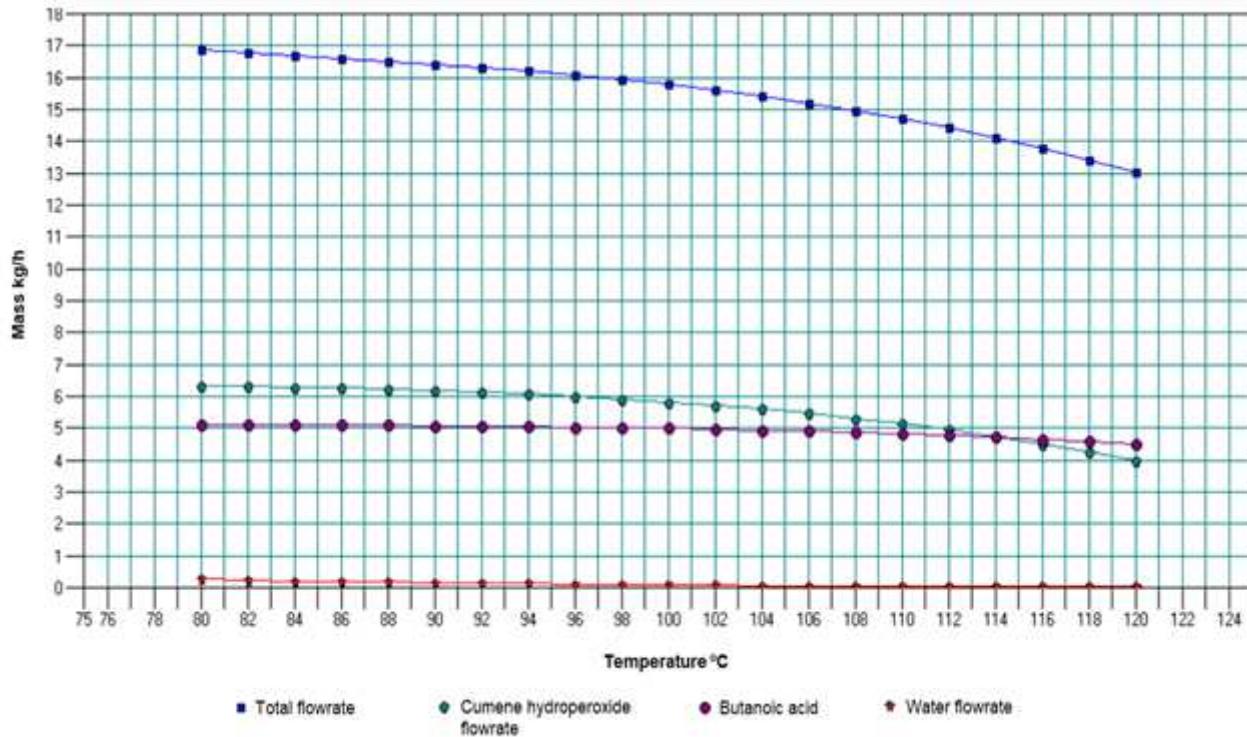


Figure 5

Sensitivity analysis for the first (primary) condenser

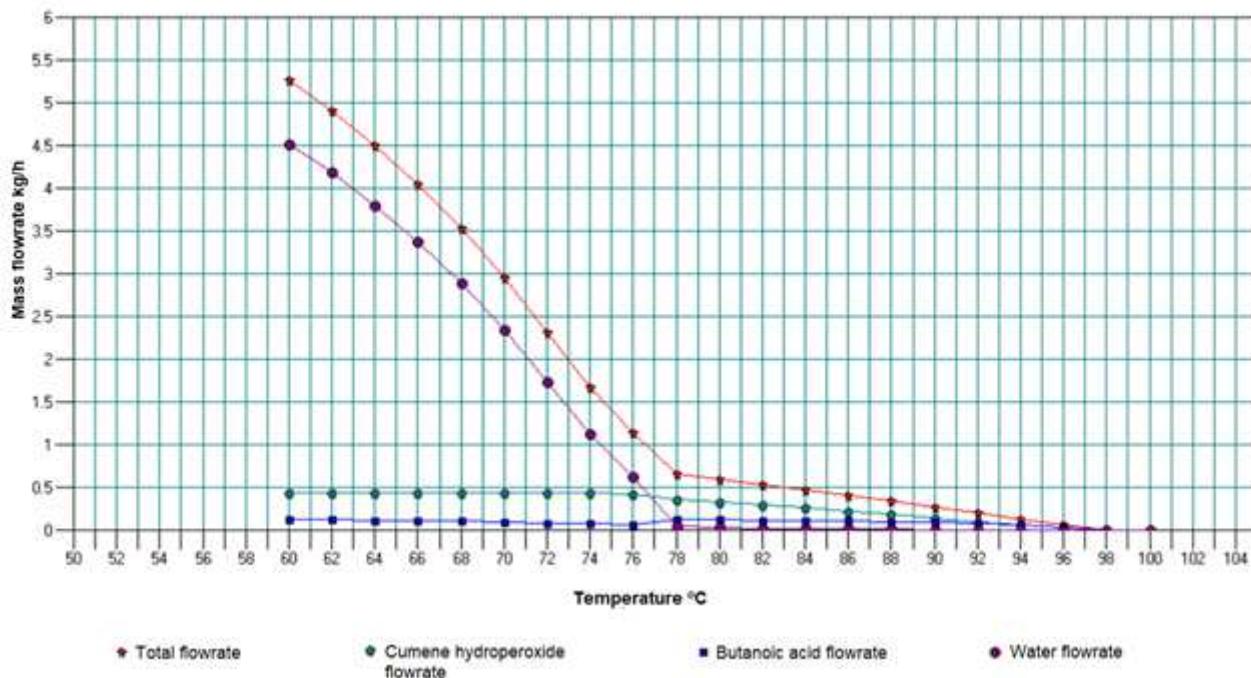


Figure 6

Sensitivity analysis for the secondary condenser, at 96°C primary condenser temperature

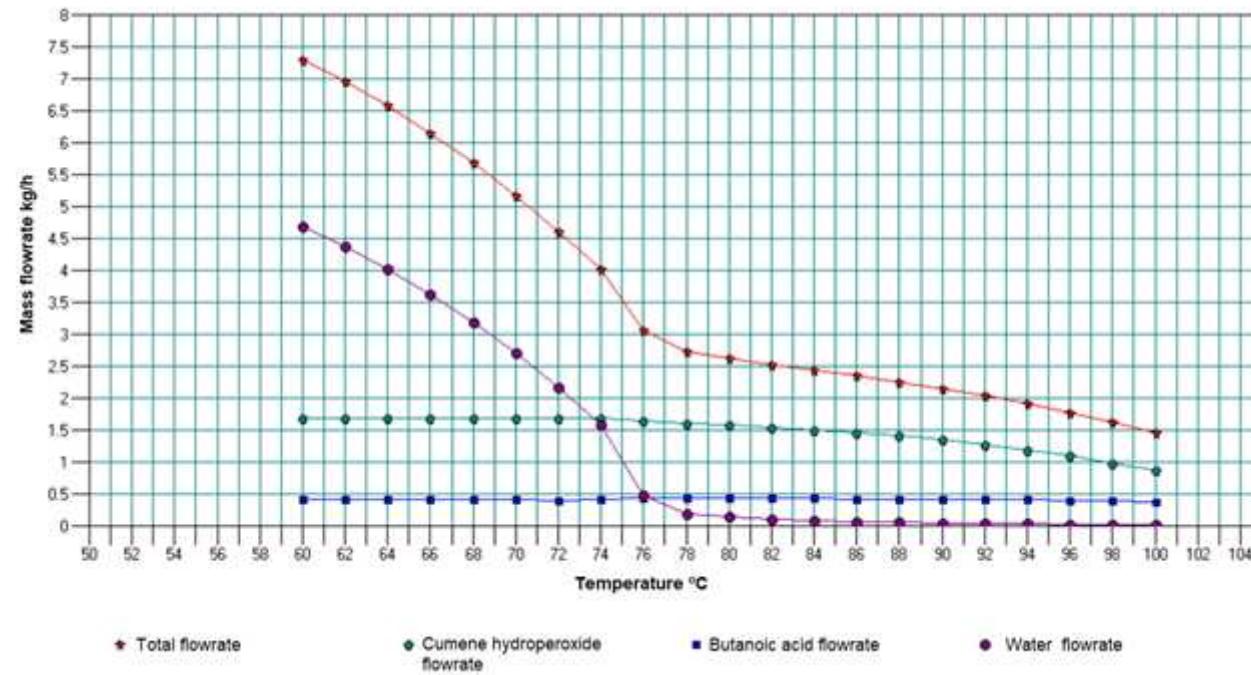


Figure 7

Sensitivity analysis for the secondary condenser at 114°C primary condenser temperature.

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