

CZECH TECHNICAL UNIVERSITY IN PRAGUE

FACULTY OF MECHANICAL ENGINEERING

The Department of Process Engineering

**BALANCE OF PYROLYSIS
FOR LIGNOCELLULOSIC WASTES**

MASTER'S THESIS

Author: Bc. Jan PAPOUŠEK

Study program: Mechanical Engineering

Specialization: Process Engineering

Supervisor: doc. Ing. Lukáš KRÁTKÝ, Ph.D.

Prague 2019

I. OSOBNÍ A STUDIJNÍ ÚDAJE

Příjmení:	Papoušek	Jméno: Jan	Osobní číslo: 437087
Fakulta/ústav:	Fakulta strojní		
Zadávací katedra/ústav:	Ústav procesní a zpracovatelské techniky		
Studijní program:	Strojní inženýrství		
Studijní obor:	Procesní technika		

II. ÚDAJE K DIPLOMOVÉ PRÁCI

Název diplomové práce:
Bilance pyrolýzy odpadů s lignocelulózovým základem

Název diplomové práce anglicky:
Balance of pyrolysis for lignocellulosic wastes

Pokyny pro vypracování:
1) Zpracujte rešerši zaměřenou na současné trendy zpracování odpadů pomocí pyrolýzy, diskutujte současné trendy a ohodnoťte je pohledem strojního inženýra.
2) Navrhněte model pyrolýzy vybraného odpadu a proveďte potřebné hmotové bilance a ověřte energetickou soběstačnost procesu.
3) Diskutujte aplikační potenciál uplatnění pyrolýzy při zpracování odpadů.

Seznam doporučené literatury:
Podle pokynů vedoucího práce.

Jméno a pracoviště vedoucí(ho) diplomové práce:
doc. Ing. Lukáš Krátký, Ph.D., ústav procesní a zpracovatelské techniky FS

Jméno a pracoviště druhého(ho) vedoucí(ho) nebo konzultanta(ky) diplomové práce:

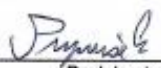
Datum zadání diplomové práce: **23.04.2019** Termín odevzdání diplomové práce: **07.06.2019**

Platnost zadání diplomové práce: _____

 _____ doc. Ing. Lukáš Krátký, Ph.D. podpis vedoucí(ho) práce	 _____ prof. Ing. Tomáš Jirovt, Ph.D. podpis vedoucí(ho) ústav/katedry	 _____ prof. Ing. Michael Valášek, DrSc. podpis děkana(ky)
---	--	--

III. PŘEVZETÍ ZADÁNÍ

Diplomant bere na vědomí, že je povinen vypracovat diplomovou práci samostatně, bez cizí pomoci, s výjimkou poskytnutých konzultací. Seznam použité literatury, jiných pramenů a jmen konzultantů je třeba uvést v diplomové práci.

30-04-2019 
Datum převzetí zadání Podpis studenta

STATEMENT OF ORIGINALITY

I hereby declare that the present master's thesis was composed by myself and that the work contained herein is my own and that all the assistance received in preparing this thesis and sources have been acknowledged.

Prague

.....

Jan Papoušek

ACKNOWLEDGMENT

I would like to express my greatest thankfulness to my supervisor doc. Ing. Lukáš Krátký, Ph.D. for his immense advice and guidance he provided to me while working on this thesis and also for him taking part in our travel to pyrolysis plant in the Netherlands.

I would also like to state my great thankfulness to Mr. Gerhard Muggen from BTG BioLiquids B.V. for his allowance to visit pyrolysis plant in the Netherlands and giving me a lecture on pyrolysis topic.

I would like to express my gratefulness to Ing. et Ing. Kateřina Svobodová from Unipetrol výzkumně vzdělávací centrum, a.s. for analysis of pyrolysis oil sample and providing me with interesting articles and data.

Let me also thank doc. Ing. Radek Šulc, Ph.D. for our occasional conversations about this topic and also for accompanying us to the Netherlands.

Acknowledgment also goes to prof. Ing. Pavel Šafařík, CSc. for arousing interest in the topic of thermodynamics and processes during his lectures.

My grateful thanks and acknowledgment also goes to my closest family for their financial aid during my whole studies and keeping me motivated for so long-time period.

At last, let me state a great thanks to my girlfriend for her mental never-ending support during my work on this thesis.

ANNOTATION

- Jméno autora: Bc. Jan PAPOUŠEK
- Název BP: Bilance pyrolýzy odpadu s lignocelulózovým základem
- Anglický název: Balance of pyrolysis for lignocellulosic wastes
- Rok: 2019
- Studijní program: N2301 Strojní inženýrství
- Obor studia: 3909T012 Procesní technika
- Ústav: Ústav procesní a zpracovatelské techniky
- Vedoucí BP: doc. Ing. Lukáš KRÁTKÝ Ph.D.
- Bibliografické údaje: počet stran 64
počet obrázků 23
počet tabulek 6
počet příloh 3
- Klíčová slova: pyrolýza, biomasa, model, process flow diagram, balance
- Keywords: pyrolysis, biomass, model, process flow diagram, balance
- Anotace: Tato práce obsahuje rešerši o odpadovém hospodářství, procesu pyrolýzy a jeho technickém řešení. Je zde popsán vytvořený model popisující zpracování odpadu s lignocelulózovým základem metodou pyrolýzy a pro účel práce je nakresleno schéma technologie s procesními jednotkami a hmotnostními a energetickými proudy. Součástí práce je analýza vzorku pyrolýzního oleje.
- Abstract: This work contains research on the topic of waste treatment, pyrolysis process and its technical solution. A model describing lignocellulosic waste processing by pyrolysis technology is developed. A process flow diagram is drawn, consisting of process units and mass and energy streams. Analysis of pyrolysis oil sample is also included in the work.

CONTENT

NOMENCLATURE.....	1
1 INTRODUCTION.....	3
1.1 Thesis purpose.....	3
1.2 Methodology	3
1.3 Introduction to waste problematics	3
1.4 Waste treatment possibilities.....	5
1.4.1 Landfilling.....	5
1.4.2 Recycling.....	6
1.4.3 Composting	6
1.4.4 Incineration technology.....	6
1.4.5 Pyrolysis technology	7
1.4.6 Gasification technology.....	7
2 THESIS PURPOSE AND ACTUAL TRENDS	8
2.1 Objects of thesis	8
2.2 The actual state of pyrolysis.....	8
2.2.1 Suitable raw material.....	8
2.2.2 Reported functional biomass pyrolysis plants.....	9
3 THEORETICAL BACKGROUND OF PYROLYSIS	11
3.1 Pyrolysis reaction	11
3.1.1 Competing model	11
3.1.2 Secondary cracking model	12
3.1.3 Active cellulose model.....	13
3.1.4 Active biomass model.....	13
3.1.5 Semi-global model	13
3.1.6 Parameters of reactions	14
3.1.7 Model summary.....	15
3.2 Pyrolysis products	15
3.2.1 Char.....	15
3.2.2 Pyrolysis gas.....	16
3.2.3 Pyrolysis oil.....	16
3.3 Types of pyrolysis	16
3.4 Pyrolysis reactors	17
3.4.1 Bubbling fluid bed reactor.....	18
3.4.2 Circulating fluidized bed reactor.....	19
3.4.3 Screw reactor.....	20

3.4.4	Rotating cone reactor	21
3.5	Pyrolysis schemes	21
3.5.1	Georgia Tech entertained bed process.....	22
3.5.2	Waterloo flash pyrolysis process.....	23
3.5.3	Ensyn process.....	24
3.5.4	BTG process.....	25
4	DEVELOPMENT OF PYROLYSIS MODEL	26
4.1	Feedstock choice	26
4.2	Technology description	26
4.2.1	Drying section	28
4.2.2	Pyrolysis section.....	29
4.2.3	Oil section	30
4.2.4	Combustion section	31
4.3	Model setup.....	32
4.4	Process units balance calculations.....	34
4.4.1	Dryer T-101.....	34
4.4.2	Condenser K-301.....	37
4.4.3	Combustion chamber D-401	38
4.4.4	Pyrolysis reactor K-201.....	43
4.4.5	Sand cooler W-401	43
4.5	Energy supply for pyrolysis reaction.....	44
4.6	Critical moisture.....	45
5	PYROLYSIS OIL ANALYSIS AND DISCUSSION.....	46
5.1	Pyrolysis oil analysis.....	46
5.2	Pyrolysis oil application.....	48
6	CONCLUSION	51
	REFERENCES.....	52
	LIST OF FIGURES.....	62
	LIST OF TABLES	63
	LIST OF ANNEXES.....	64
	Annex 1: Mass and energy balances	
	Annex 2: Critical moisture	
	Annex 3: Process flow diagram	

NOMENCLATURE

Symbol	Quantity	Unit
A	pre-exponential factor	s^{-1}
c^n	mole percent	%
c^m	mass percent	%
c	specific heat capacity	$J/(kg \cdot K)$
c_p	specific heat capacity at constant pressure	$J/(kg \cdot K)$
E_A	activation energy	$J/(mol \cdot K)$
h	specific enthalpy	J/kg
h^R	specific reaction enthalpy	J/kg
k	reaction rate	s^{-1}
LHV	lower heating value	$J/kg; J/Nm^3$
m	mass; mass flow	$kg; kg/s$
M	molar mass	g/mol
p	pressure	Pa
Q	heat power	W
R	gas constant	$J/(mol \cdot K)$
t	time	s
T	temperature	$^{\circ}C$
V	volume; volume flow rate	$m^3; m^3/s$
w	water content in solid material	%
x	water content in dry air	kg/kg
λ	excess ratio	-

Subscript

Meaning

A	reactant A
AIR	air
AMB	ambient, surroundings
ASH	content of ash

ASHB	content of ash after biomass burnout
ASHC	content of ash after char burnout
B	biomass after reaction; product B
BDRYER	biomass at dryer output
BFEED	biomass at feed input
C	char
CH ₄	methane
CIRC	circulating
CO	carbon monoxide
COOL	cooler
COMB	combustion
COND	condensation
DRYER	dryer
FLUEGAS	fluegas
G	pyrolysis gas
H ₂	hydrogen
IN	input
L	pyrolysis oil
LCOOL	pyrolysis oil aftercooler
O ₂	oxygen
O ₂ AIR	mole percent of oxygen in air
OUT	output
PYRO	pyrolysis
REAC	reaction
SAND	sand
W	water
1W	water removed by 1 kg/h of air

1 INTRODUCTION

1.1 Thesis purpose

The aim of this work is to gather information about available pyrolysis technology regarding its use as a thermochemical conversion technology to process biomass waste. Next part of this thesis is the development of a model to validate found data and calculate the mass and energy balances of the technology. A future insight into the usability of biomass waste pyrolysis and the potential for future research is proposed at the end of the thesis along with pyrolysis oil sample analysis and discussion about its utilization.

1.2 Methodology

The procedure of writing of this work starts with literature research of suitability of various waste type raw materials, an overview of available pyrolysis technology and reactor schemes as well as comparison of pyrolysis to other waste processing technologies. Literature research is followed by a patent and industrial research to find out about pyrolysis of biomass waste on the non-scientific scale. A plant inspection in Hengelo, the Netherlands takes place after investigation of running projects worldwide. The object of plant inspection and discussion with representatives of the plant is to check found data and the author's assumptions. A process flow diagram is drawn by the author. Next, a model in MATLAB based on available data and process parameters is created and required mass and energy balance calculations are proposed. Lastly, a pyrolysis oil sample analysis data are evaluated and pyrolysis oil potential is discussed.

1.3 Introduction to waste problematics

The waste production goes hand in hand with urbanization and population growth. The author suggests insight to waste production on different scales in order to confirm or disprove the increase of waste amount. Data on total waste production on a global scale are gathered and presented in Table 1 Municipal solid waste production worldwide data are not available.

Table 1: Waste production worldwide [1], [2]

Year	2002	2012	2016
Total waste production [million tonnes]	680	1300	2010

Table 2 shows total and municipal solid waste produced in the European Union.

Table 2: Waste production in the European Union [3], [4]

Year	2004	2012	2016
Total waste production [million tonnes]	2548	2484	2538
Solid municipal waste production [million tonnes]	253	245	253

Table 3 shows total and municipal solid waste produced in the Czech Republic.

Table 3: Waste production in the Czech Republic [3], [4]

Year	2004	2012	2016
Total waste production [million tonnes]	29	23	25
Solid municipal waste production [million tonnes]	2.9	3.2	3.6

The data available for comparison between the World, the European Union and the Czech Republic are not united and come with a level of uncertainty. The purpose of this section was mainly to observe the progress of waste production in term of approx. 15 years on different levels of scale. By comparing waste production data on relevant levels, a very slight decrease in the Czech Republic and the European Union can be seen, compared with a huge increase on a global scale. The author would like to note, that even though the waste produced in the European Union and the Czech Republic could be considered as steady, over half of all the waste in the EE is being landfilled (see Figure 1), leading to an unavoidable accumulation of waste. This statistic might serve as a motivation to waste problematics.

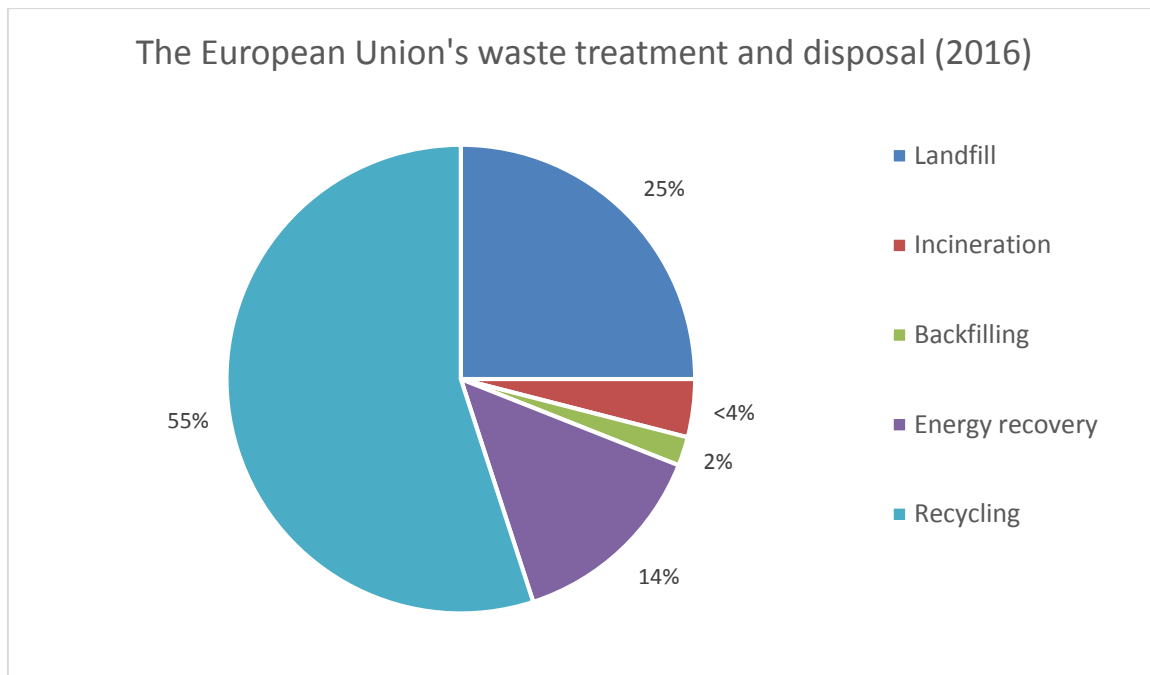


Figure 1: Waste treatment and disposal in the European Union [5]

1.4 Waste treatment possibilities

As was shown in the chapter above, waste generation is either rising or at least isn't decreasing. This deserves a solution in terms to further process generated waste. Appropriate technology must be chosen based on the type of waste, its amount, technological possibilities in a given location, etc. From the author's point of view, waste treatment technologies can be divided into four main groups: landfill, recycling, composting and thermochemical conversion. Thermochemical conversion methods can be further divided as follows: incineration, gasification, and pyrolysis. These technologies are used to thermochemically convert waste and utilize it. Process parameters – temperature and amount of oxygen may differ.

1.4.1 Landfilling

Landfilling is a process of burying waste underneath the ground [6]. According to estimations, about 40 % of all produced waste is stored in landfills. This material has little or no further chance of being reused, while also pollution of water resources and the air was reported [7]. This solution might appear as the most easily approachable, however, due to

the continual filling of land with waste and little or no further waste usage, this technology can't serve as a final solution. According to the Circular Economy Package adopted by the European Commission, a maximum of 10 % of all municipal waste will be allowed to be landfilled in member states of the European Union by 2035 [8].

1.4.2 Recycling

Recycling of rare metals and metals with higher economic value is often a requirement of economically sustainable technology, e.g. re-use of the platinum catalyst in nitric acid production [9]. Recycling of main waste types such as plastics, glass, and paper is a usual way of dealing with waste. According to [10], 20 % of total plastic waste was recycled in 2015 globally. This number depends on political pressure, citizens willingness in given country and state of the waste recycling market. According to the Circular Economy Package adopted by the European Commission, 65 % of municipal waste shall be recycled in member states of the European Union by 2030 [8].

1.4.3 Composting

Composting of biomass waste is known in household-scale as well as industrial scale, either open-air windrow composting or in-vessel composting. These methods are used to reduce the amount of biomass waste while creating compost that can be used in soil remediation [11].

1.4.4 Incineration technology

Incineration is an exothermic process, that might be applied to e.g. municipal solid waste or biomass. Direct combustion of biomass is technologically well-known compared to pyrolysis or gasification plant. Usually, excess air is used to improve the incineration process. Flue gas as an output of the process is present at high temperature (800 °C) and is used as a heat carrier for follow-up process as a direct heating or electricity generation with either gas or steam turbine [12].

1.4.5 Pyrolysis technology

Pyrolysis, an endothermic process, takes place at increased temperature (400-900 °C) with little or no air access and results in the production of char, condensable and incondensable gases [13]. After char removal and gas quenching, three products of the reactions can be observed, namely: char (solid phase), condensed pyrolysis oil (liquid phase) and incondensable pyrolysis gas (gas phase). The yield of products depends on the type and quality of input material as well as process parameters in the reactor – mostly temperature and time of reaction.

1.4.6 Gasification technology

Gasification, an endothermic process, takes place at a higher temperature during the process (1000 – 1500 °C), resulting in a higher yield of gas compared to pyrolysis. Four stages in the gasifier can be observed, namely drying, pyrolysis, combustion, and reduction. During the combustion phase, the process takes advantage of so-called partial oxidation, that can be described as obtaining required energy for the following process thanks to the combustion of biomass which releases heat. Partial oxidation requires air input, generally a sub-stoichiometric amount [13], [14], [15].

2 THESIS PURPOSE AND ACTUAL TRENDS

2.1 Objects of thesis

This paper is composed of research part, model part, and sample analysis. Aim of the research part is to:

- State different types of pyrolysis in terms of the type of input material and carry on with the one that is mostly used in nowadays industry of energy recovery of waste.
- Compare pyrolysis waste treatment to other available technologies and show the advantages and disadvantages of such an approach.
- State different types of pyrolysis unit operation schemes and reactors.
- Give an example of an industrial scale running project.

Aim of the model is to:

- Create a process scheme based on industrial application research.
- Apply similar process parameters and reactor type.
- Define the suitable type and quality of input material.
- Verify the model based on data collected during research.
- State of the model should allow to easily redefine input material amount and properties as well as main process parameters in process units.

Sample analysis should provide insight on these topics:

- Pyrolysis oil elementary composition.
- Properties evaluation, such as density, heating value, etc.
- Based on previous information, the potential of pyrolysis oil in refinery sector is discussed.

2.2 The actual state of pyrolysis

2.2.1 Suitable raw material

There are several reported types of material that might be suitable for pyrolysis. Wood and woodworking industry residual waste was reported as the oldest input material used by

mankind [16]. Another source of biomass might be agricultural crops residues and by-products such as shives, straw, husks, pits, etc. [17]. Usability of pyrolysis to process waste tires has also been reported [18]. Pyrolysis might be used to break down molecules of plastics. However, great technical difficulties have been noted, such as solidification of wax during the processing, leading to a build-up of material inside of process pipelines, thus decreasing overall performance. Another reported problem is a decrease of pyrolysis oil properties if a mixture of plastics (HDPE, LDPE, PP, PS, PVC, ...) is used rather than input composed of only one plastic-type. During pyrolysis of PVC, hydrogen chloride is released and its toxic vapors must be collected and eliminated before causing any harm [19]. As far as the author can tell, only one successful implementation of a commercial-scale plant of municipal plastic waste is reported from Sapporo, Japan with a capacity of 50 tons of mixed plastics daily [20].

To sum it up, the greatest success with pyrolysis is to eliminate biomass waste from various resources. Most of the laboratory measurements that were found by the author during research take a closer look at wood and its residuals. Some data may be found about other biomass types, mainly from agricultural waste. According to [21], biomass pyrolysis plant runs best after a series of tests on given raw material and the stock type and quality should remain the same during the lifecycle of the plant. When it comes to choosing with which type of biomass should a plant be operated, parameters such as availability, cost of feedstock, the performance of the material in pyrolysis laboratory tests, etc. must be taken into account [17].

2.2.2 Reported functional biomass pyrolysis plants

This chapter contains information about currently running biomass pyrolysis plants at commercial scale and some technical parameters of these applications. In Hengelo, the Netherlands, a facility was built by BTG-BTL company and is currently run by Twence Holding B.V. It was commissioned in 2015, producing approx. 3.3 t/h of pyrolysis oil at 5 t/h of wood chips feedstock with the aim to achieve production of 20 millions liters of pyrolysis oil per year. The unit uses a rotating cone reactor with sand as a heat carrier. In May 2019, construction of pyrolysis plant with similar parameters by the same company in Lieska, Finland was announced [22].

In 2013, pyrolysis plant in Joensuu, Finland was constructed by Fortum company. Based on the fluidized bed reactor, the facility is able to produce 50 000 tons of oil annually by using 100 000 tonnes of wood each year [23].

The facility in Ontario, Canada, was commissioned in 2006 with designed production of 11 millions liters of pyrolysis oil per year. In 2014, other add-ons were announced to increase the production as well as aim to present the oil to the refinery co-processing in 2017. In this technology, sand is used as a heat carrier in a fluidized bed reactor with recycled pyrolysis gas as the draft force [24].

3 THEORETICAL BACKGROUND OF PYROLYSIS

3.1 Pyrolysis reaction

Pyrolysis is a series of reactions that take place at an increased temperature at an oxygen-free atmosphere or at atmosphere with a reduced amount of oxygen. Chemical formulas of reactions with biomass type of material are not stated, as it greatly depends on conditions and amount of cellulose, hemicellulose, and lignin in a given type of biomass feed. Various models describing the decomposition of biomass into certain products can be found in the literature. The overall idea of decompositions found in literature is the following: Reactions may be considered as primary or secondary. During primary reactions, biomass may be decomposed into three possible phases, namely solid, liquid and gas. During secondary reactions, tars from primary reactions (that is further condensed into pyrolysis oil) may further decompose into any pyrolysis gas or char [25]. Based on these models, many authors make laboratory measurements and determine constants for a given model such as activation energy, enthalpy of reaction, etc. Following chapters shall introduce some of these models.

3.1.1 Competing model

This empirical model doesn't aim to describe the reactions in terms of primary and secondary, it only tells us about final composition of products, namely char, tar (liquid) and gas [26], [27]. A scheme can be seen in Figure 2. Advantage of this model is its simplicity. However, it doesn't closely describe any certain reaction, rather than just the final composition [28].

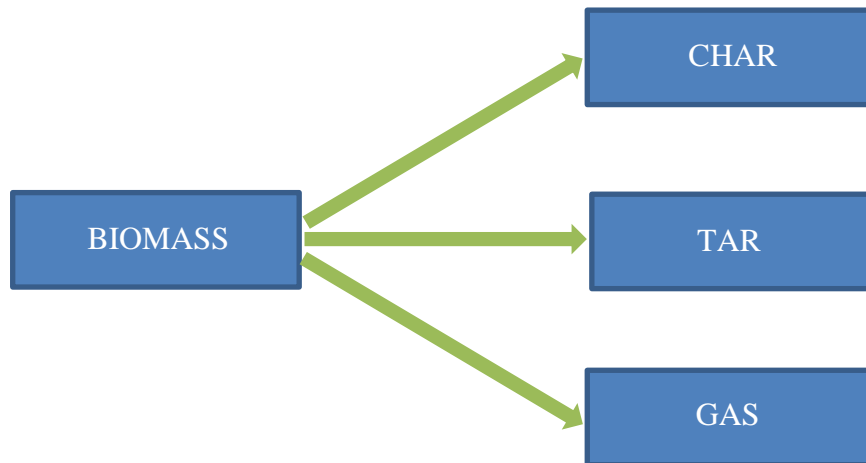


Figure 2: Competing model scheme

3.1.2 Secondary cracking model

This model suggested by [29] and used in work by [30] introduces three primary parallel reactions that crack biomass into char, tar (liquid) and gas. Tar is further cracked into gas and char by two secondary reactions. A scheme can be seen in Figure 3.

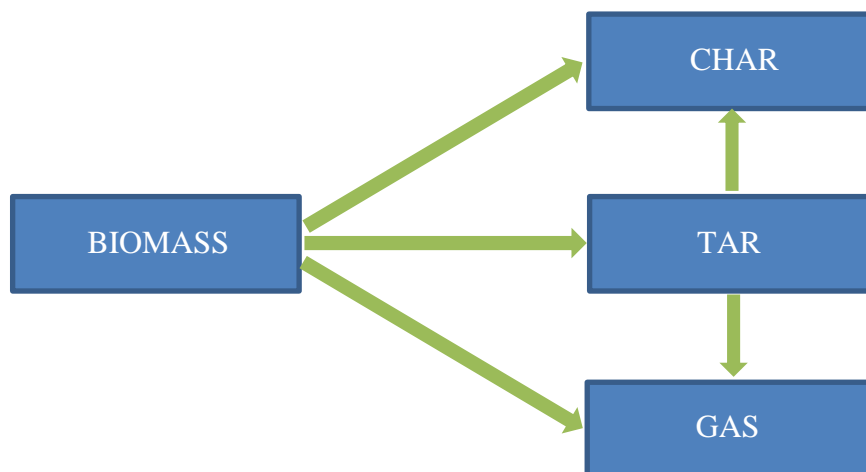


Figure 3: Secondary cracking model

3.1.3 Active cellulose model

As was shown by [31], cellulose – one of three components of biomass – decomposes not directly towards pyrolysis products, it rather takes an intermediate step by transformation into so-called active cellulose at low temperatures. Furthermore, active cellulose is a reactant in two competing reactions, one of them results in the creation of char and gas, while the second one results in tar (liquid) formation. In [32] a follow-up reaction was suggested, further cracking tar (liquid) into gas. A scheme is shown in Figure 4.

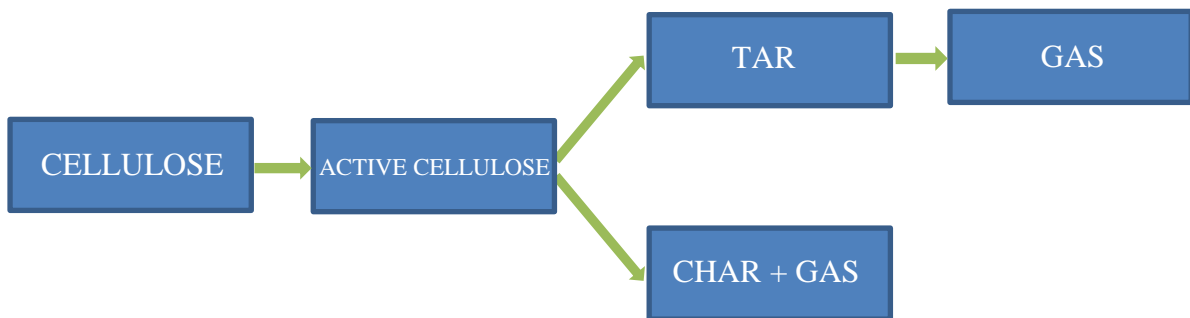


Figure 4: Active cellulose model

3.1.4 Active biomass model

A simple improvement to active cellulose model (see Chapter 3.1.3) was proposed by [33], [34]. Active cellulose is substituted with active biomass or so-called intermediate, while the model scheme remains the same and is used to describe not only the cellulose part of the biomass sample but the material as a whole.

3.1.5 Semi-global model

Proposed by [35], this model takes advantage of dividing biomass into three pseudo-components, which aren't based on their chemical composition but on laboratory measurements corresponding with the proposed scheme (see Figure 5). Every pseudo-component has its own kinetic reaction formulas that describe its decomposition into gas, char or intermediate solid that further decomposes into gas and char.

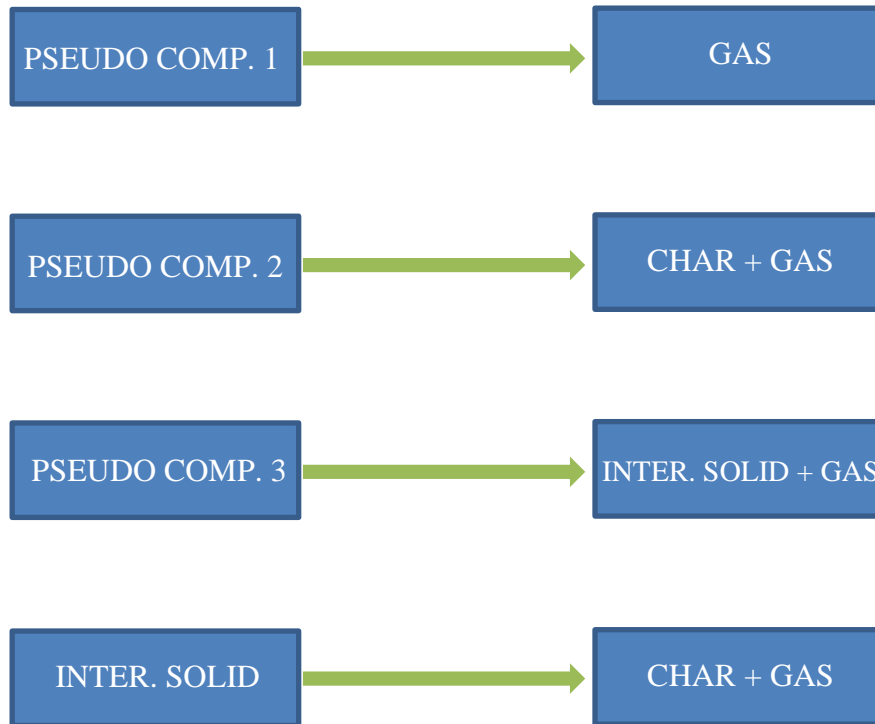


Figure 5: Semi-global model

3.1.6 Parameters of reactions

Let's assume a simple reaction as shown in Figure 6. Reactant A is being transformed into product B due to the rate of chemical reaction k . Following ordinary differential equation can be used to mathematically formulate change of reactant's A mass m_A depending on time t :

$$\frac{dm_A}{dt} = -k \cdot m_A. \quad (1)$$



Figure 6: Reaction example

Following reaction can be used to describe the build-up of product B:

$$\frac{dm_B}{dt} = k \cdot m_A, \quad (2)$$

where k is the reaction rate, which can be further described using so-called Arrhenius equation, that shows the dependence of reaction rate k on temperature T [36]:

$$k = A \cdot \exp\left[-\frac{E_A}{R \cdot T}\right]. \quad (3)$$

Constants A and E were gathered in work by [37].

3.1.7 Model summary

Many authors proposed various models that may be used to describe pyrolysis biomass reaction with parameters determination after a series of laboratory tests and measurements. According to [28], models that consider secondary liquid (tar) cracking usually describe the reactions better, as considering only primary cracking results in too optimistic pyrolysis oil yield. In Chapter 4.3, dedicated to material and energy balance calculations, the author used the secondary cracking model, with parameters taken from the work by [38], [39], [32]. The script is ready to change parameters easily or the whole model scheme might be changed with only minor changes required in the programmed script.

3.2 Pyrolysis products

During pyrolysis, three main products are formed, namely char, incondensable gases, and condensable gases forming pyrolysis oil. This chapter aims to briefly describe some key characteristics of these products.

3.2.1 Char

Char or biochar is a solid product of biomass pyrolysis. To get higher yields of char, longer resident times and lower temperatures are preferred. With higher temperatures, the carbon

content in char increases, while oxygen and hydrogen content decreases [40]. The typical range of yield as a percentage of dry biomass input varies from 10 up to 40 % [41]. The possible potential of char is as fertilizer or as fuel with a reported lower heating value of 27.5 MJ/kg [42].

3.2.2 Pyrolysis gas

Term pyrolysis gas is used to name the gas phase that remains after pyrolysis reaction takes place and output gas is cooled, partly condensed. Non-condensable gases (at temperatures around 20-60 °C) from this process are called pyrolysis gas. The typical composition consists of methane CH₄, hydrogen H₂, carbon monoxide CO and carbon dioxide CO₂ [13]. Reported lower heating value is around 10 MJ/Nm³, highly depending on gas composition. Possible usage of pyrolysis gas is being burned as fuel, optimally right in the pyrolysis plant facility, due to its gas state which is not very suitable for longer transport. The typical range of yield as a percentage of dry biomass input varies from 20 up to 40 % [41].

3.2.3 Pyrolysis oil

Pyrolysis oil is liquid output from the condenser of pyrolysis gases after the process of pyrolysis itself took place in the reactor. It is a viscous brown liquid consisting of 300 to 400 compounds with a pH around 3 [43], [44]. Its typical range of yield as a percentage of dry biomass input from 30 up to 70 % [41]. Properties of pyrolysis oil sample along with a discussion of its potential are further discussed in Chapter 5.

3.3 Types of pyrolysis

Process of pyrolysis can be divided in terms of the residence time. This comes hand in hand with a temperature of the process. For longer residence time, lower temperatures are sufficient. For shorter residence time, the temperature of the process must be higher. Pyrolysis process can be therefore divided into three groups:

- Slow pyrolysis – from 5 to 30 minutes at temperatures from 400 to 500 °C. Formation of char is greatest compared to other types of pyrolysis.
- Fast pyrolysis – in terms of seconds, up to tens of seconds at temperatures from 450 to 600 °C. This favors build-up of pyrolysis oil.
- Flash pyrolysis – tenths of seconds up to 2 seconds at temperatures from 500 to 800 °C. Creation of pyrolysis gas is favored in this case [13].

3.4 Pyrolysis reactors

The reactor is a very important process unit in the whole plant setup. This chapter should provide a list of popular reactor types.

3.4.1 Bubbling fluid bed reactor

One of the possible modifications of the fluidized bed reactor is the bubbling one. Biomass, dried and crushed to 2-3 mm particles size enters a zone, where hot sand is fluidized by gas and heat is supplied to the reactor. During the reaction, biomass particles decrease in size and together with produced gas are drafted out of the reactor zone. Pyrolysis gas recycle can be used as a fluidizing medium, to ensure an oxygen-free atmosphere. The scheme can be seen in Figure 7. Construction and operation are simple, but no industrial-scale application is running at the time. Company Dynamotive ran two reactors of these types in Canada, however, both were already dismantled, as some problems with heat transfer occurred [45].

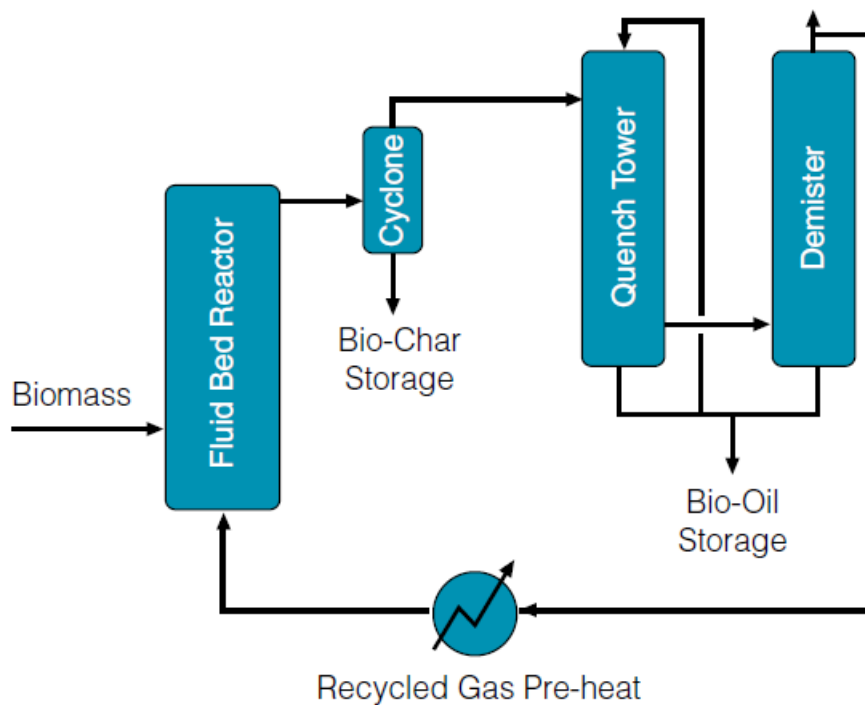


Figure 7: Bubbling fluid bed reactor scheme [46]

3.4.2 Circulating fluidized bed reactor

This reactor is a second possible modification of the fluidized bed reactor. It differs from the bubbling fluidized bed reactor (see Chapter 3.4.1) due to the circulation of the transport medium, usually sand. Biomass and forming char are transported as well as sand into a burner, where char and biomass are burned, leading to heating of sand which is then recirculated into the reactor. Gases are usually separated before burner in cyclones [45], [47]. A scheme can be seen in Figure 8. Ensyn pyrolysis plant in Canada runs with this type of reactor at 4 t/h feed [48].

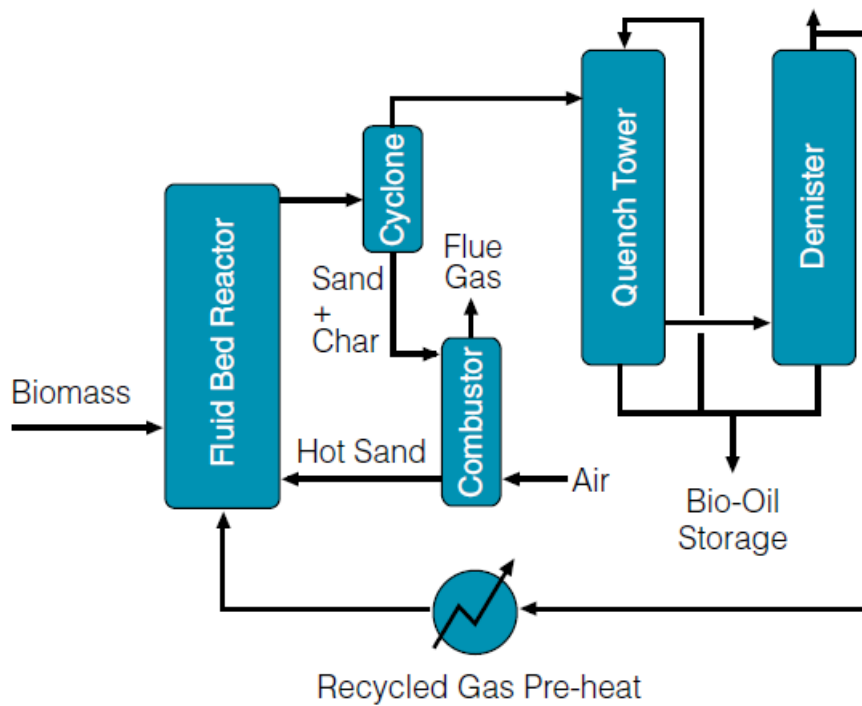


Figure 8: Circulating Fluidized Bed Reactor scheme [49]

3.4.3 Screw reactor

In this type of reactor, biomass is moved through the heated zone not by fluid, but by mechanical screw. As a heating source, hot sand or hot steel balls can be used. Residence time can easily be adjusted by the rotary speed of the screw, also no carrier gas is necessary. The mechanical design must be considered very carefully, as mechanical wear and tear may take place. This application is popular for small size inputs, as the scaling of screw might face some mechanical design problems with the system for rotation movement [50]. A conceptual scheme is shown in Figure 9. Abritech pyrolysis plant in Canada runs with this type of reactor at feed 2 t/h [48].

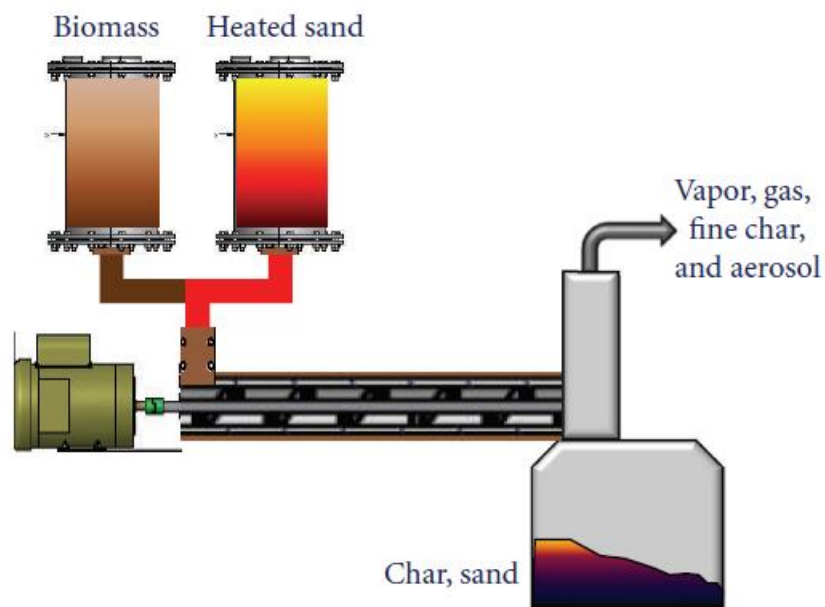


Figure 9: Screw reactor [51]

3.4.4 Rotating cone reactor

Biomass and heat carrier (usually sand) is inserted into a high-speed rotating cone. No carrier gas is required. Thanks to rotation, biomass and sand are mixed, leading to high heat transfer. Residence time can be adjusted by rotary speed settings. Afterward, all solid particles are sent to the burner, where incineration takes place together with oxygen and non-condensable pyrolysis gas. This process was reported as autonomous, in terms of energy input for the reactor. Cone rotates at approx. 600 rpm, so careful mechanical design must be assured. There are two operating industrial plants with this reactor, one with feedstock of 2 t/h, second of 5 t/h [50], [52]. Reactor design can be seen in Figure 10.

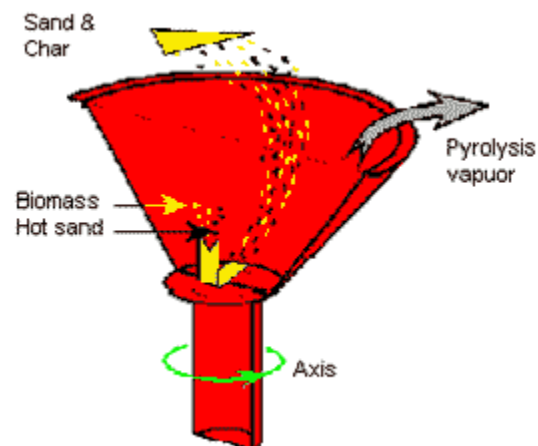


Figure 10: Rotating cone reactor design [53]

3.5 Pyrolysis schemes

This section shall provide an overview of some pyrolysis plant applications throughout the times.

3.5.1 Georgia Tech entertained bed process

This process was developed and patented by Georgia Tech company in 1986 in the United States of America [54]. Biomass crushed to a particle size of 1 mm is dried to 10 % moisture and introduced to the inert atmosphere. It is then drafted inside the reactor, where heat supply is secured by burning propane and air. Biomass particles are drafted towards reactor outlet, where char is separated, condensable gases are condensed to pyrolysis oil and non-condensable gases are burned with air in order to dry entering biomass [55]. Technology scheme can be seen in Figure 11.

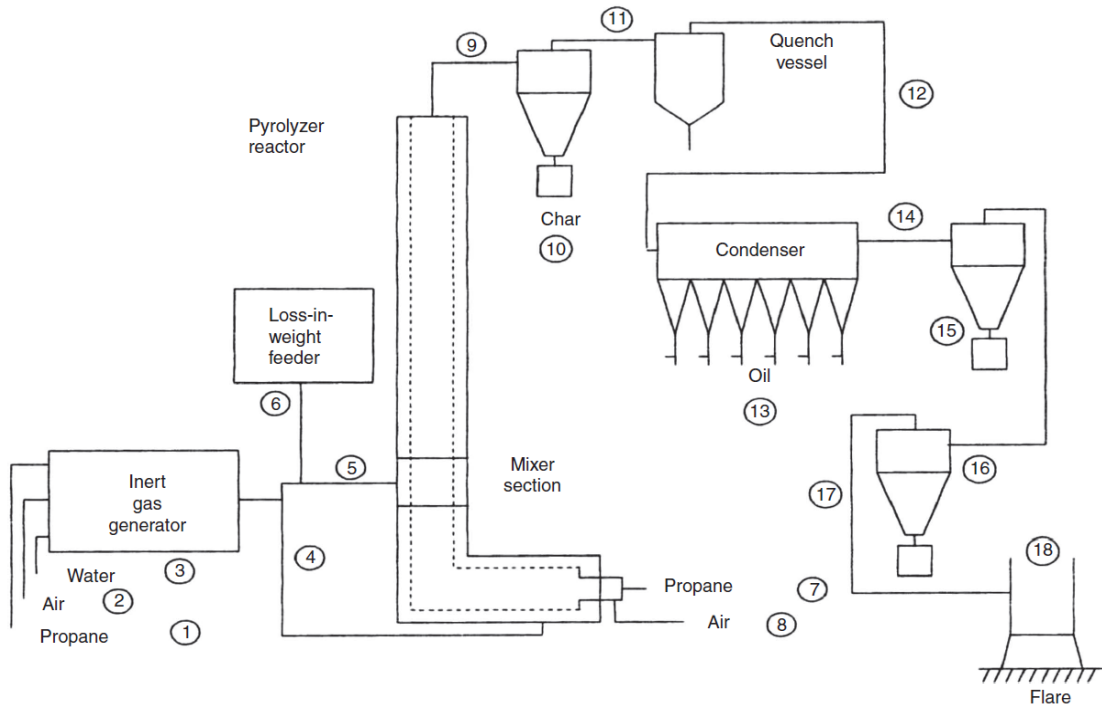


Figure 11: Georgia Tech entertained bed process scheme [56]

3.5.2 Waterloo flash pyrolysis process

This process utilizes a bubbling fluidized bed reactor (see Chapter 3.4.1). Biomass is crushed, dried and introduced to a hopper and then drafted inside the reactor by a small portion of recycle gas. Inside the reactor, hot sand is present and serves as a heat transfer medium. Heat is supplied by burning pyrolysis gas with the addition of either heating coils or burning natural gas. Char is later separated, pyrolysis oil is condensed and pyrolysis gas is burned [55], [57]. A scheme is shown in Figure 12. The idea comes from the University of Waterloo, Canada, where a 5 kg/h laboratory-scale plant was operated. Based on this scheme, a 200 kg/h pilot-scale plant was operated by Union Fenosa in Spain. The author found no evidence of this plant being operated at this very time.

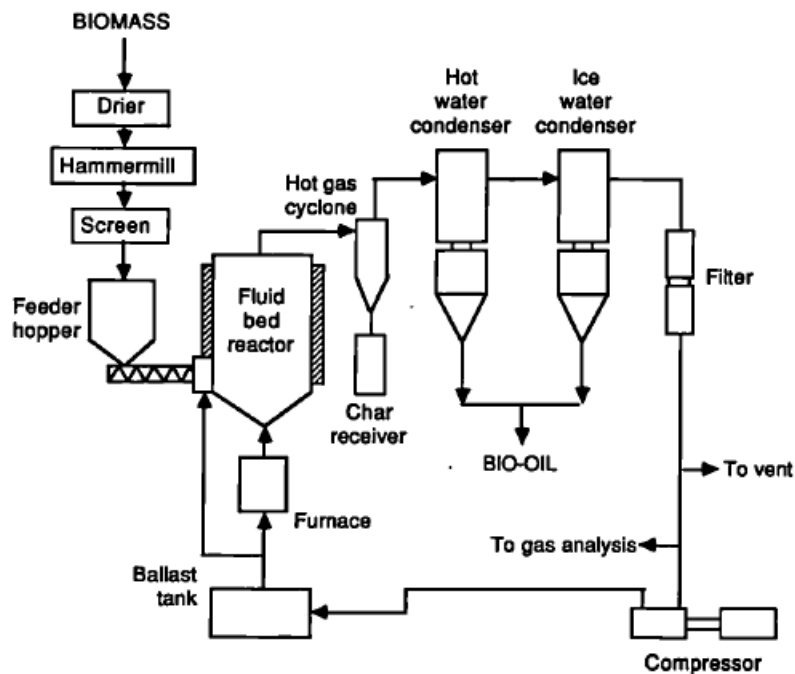


Figure 12: Waterloo flash pyrolysis process scheme [58]

3.5.3 Ensyn process

This plant takes advantage of a circulating fluidized bed reactor (see Chapter 3.4.2). Biomass is introduced into a reactor with hot sand as fluidizing and heat transfer medium. Sand is separated based on particle size, char is separated, gas is taken to condensers, where pyrolysis oil is formed and remaining incondensable gas is taken further away. Combustion of either char or pyrolysis gas is suggested by the owner of the patent, combustion of both these products together is also an option. Any required extra heat can be provided by burning natural gas. Ensyn company designed these plants in North America [13], [55], [59]. A scheme of this process is shown in Figure 13.

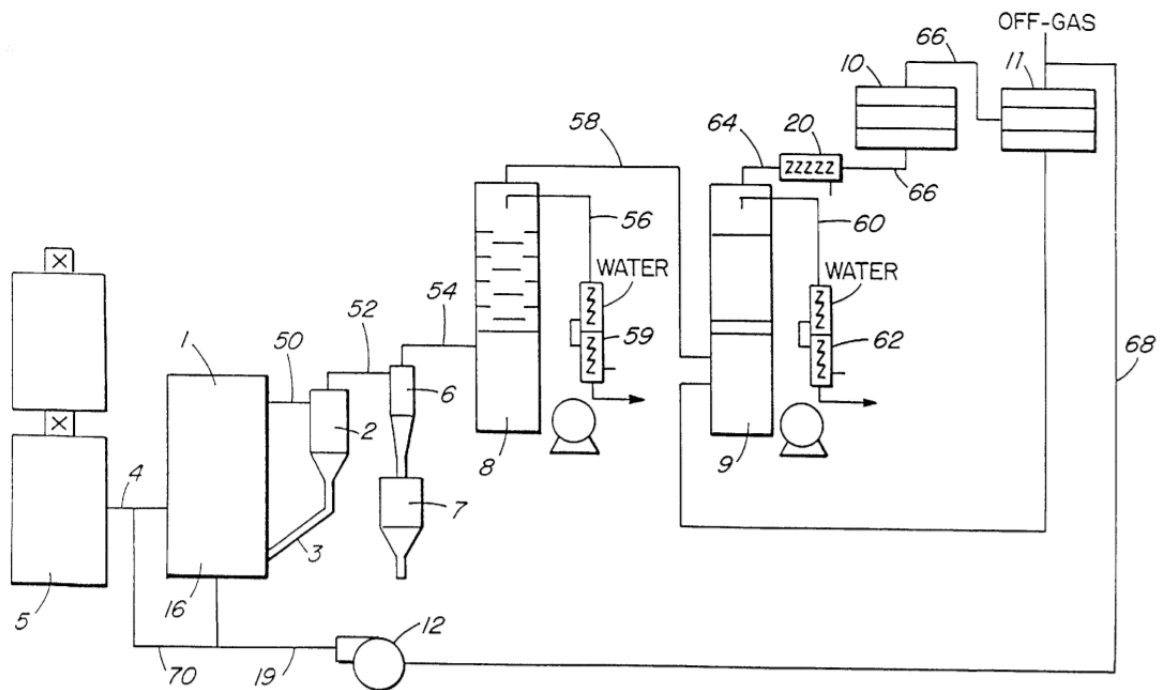


Figure 13: Ensyn process scheme [60]

3.5.4 BTG process

This process is based on an idea from the University of Twente, the Netherlands and utilizes a rotating cone reactor. Biomass, crushed and dried enters the reactor, where it mixes with hot sand. Sand and char are separated from the stream of gas, which is further cooled, partially condensed into pyrolysis oil and pyrolysis gas. Gas and char are burned, thus heating sand, which then returns to the reactor [61], [55]. One facility is currently operational and the second one is under construction, as was reported in Chapter 2.2.2. A scheme can be seen in Figure 14.

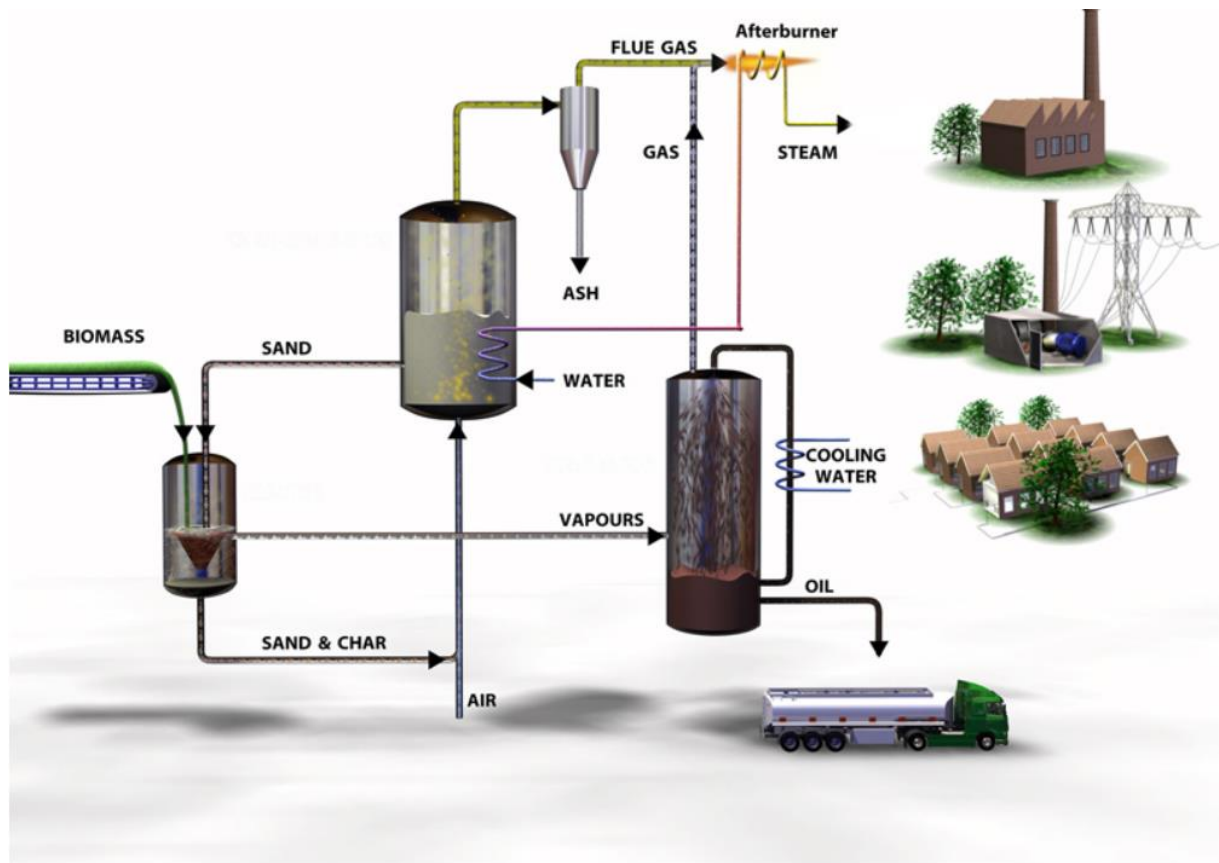


Figure 14: BTG process scheme [62]

4 DEVELOPMENT OF PYROLYSIS MODEL

This chapter describes the author's approach to create a mass and energy balance of the pyrolysis plant system. The author took advantage of process parameters either found in literature or confirmed by operators of pyrolysis plant in Hengelo, the Netherlands. The reactor itself was considered a rotating cone reactor (see Chapter 3.4.4). Following text describes the author's ideas about process flow diagram, proper process units choice and mass and energy balance of the whole system. All scripts may be found in Annex 1 and if any value or chosen pyrolysis reaction model won't be suitable for following work based on this paper, it may be easily changed to meet another author's intentions.

4.1 Feedstock choice

Author estimates, that most available laboratory data about pyrolysis feedstock is wood. Wood particles, so-called chips might serve better than wood sawdust due to their non-dust character, which is better for transportation. This type of feedstock is used in reference technological process as well as in other facilities (see Chapter 2.2.2). Particle size should be approx. 3 mm, as reported in reference technology [63]. Properties of feedstock that were used in the model are the following: moisture, heat capacity, and lower heating value. Those values may be adjusted in order to fit another feedstock, such as agricultural residues. Series of the tests to confirm the usability of certain feedstock are recommended [21], [64]. Pyrolysis unit is usually constructed based on a certain type of feedstock and no further alterations are recommended [21].

4.2 Technology description

Schematic layout of the proposed unit can be seen in Figure 15. Complete Process flow diagram scheme can be found in Annex 3. In order to ensure drawing clarity, whole technology is divided into four sections, which shall be further described in the following text:

- Drying section with input stream 1 and output stream 5.
- Pyrolysis section with input streams 5 and 15 and output streams 11 and 13.

- Oil section with input stream 11 and output stream 24.
- Combustion section with input streams 13, 24 and 25 and output streams 15 and 19.

Material and energy balance table for the assumption of 1 ton per hour input of wood chips can also be seen in Annex 3 as well as a list of process units. MATLAB scripts for material and energy balance can be seen in Annex 1.

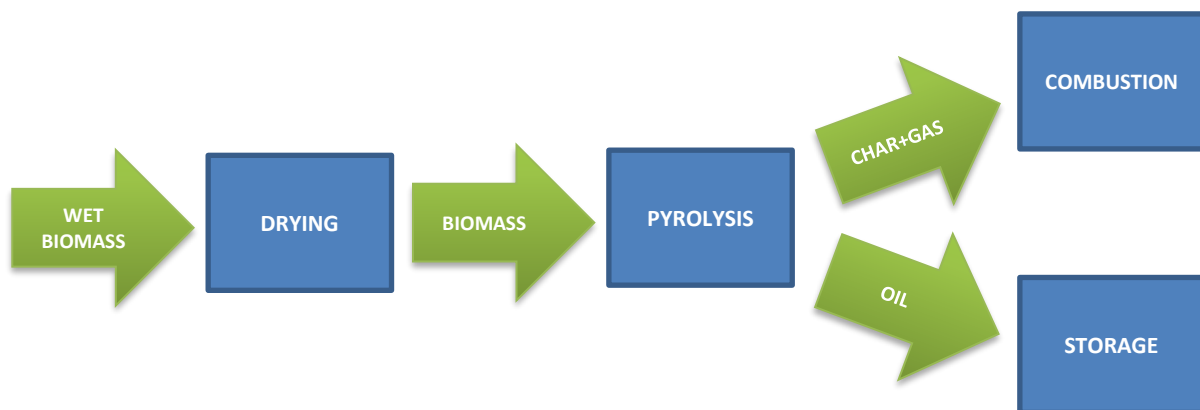


Figure 15: Proposed model block scheme

4.2.1 Drying section

Input to this section is *stream 1*, consisting of wood chips and water in the form of moisture. Wood chips are stored in vessel *K-101* to ensure operational reserve. Wood chips are then thrown at belt conveyor *H-101*, which takes them into belt dryer *T-101*. Forced draft fan *V-101* is responsible for pressurizing ambient air and blowing it to heater *W-101*, where the temperature of the air is increased thanks to *energy stream Q1* because warmer air will be further utilized to remove excess water from wood chips. This takes place in dryer *T-101*, used air with water leaves then at *stream 4*, while wood chips without excess water are present in *stream 5* and lead into screw conveyor *H-102*. Described process can be seen in Figure 16. Process of drying can be displayed in the Mollier chart as shown in Figure 21.

To make sure that this model will be functional even if proposed states of air needed to change or if some optimization would have to run, a script by Assistant Professor Amanda D. Smith from the University of Utah is used [65], [66]. Thanks to it, there is no need to repeatedly use Mollier chart for every new suggested condition of drying.

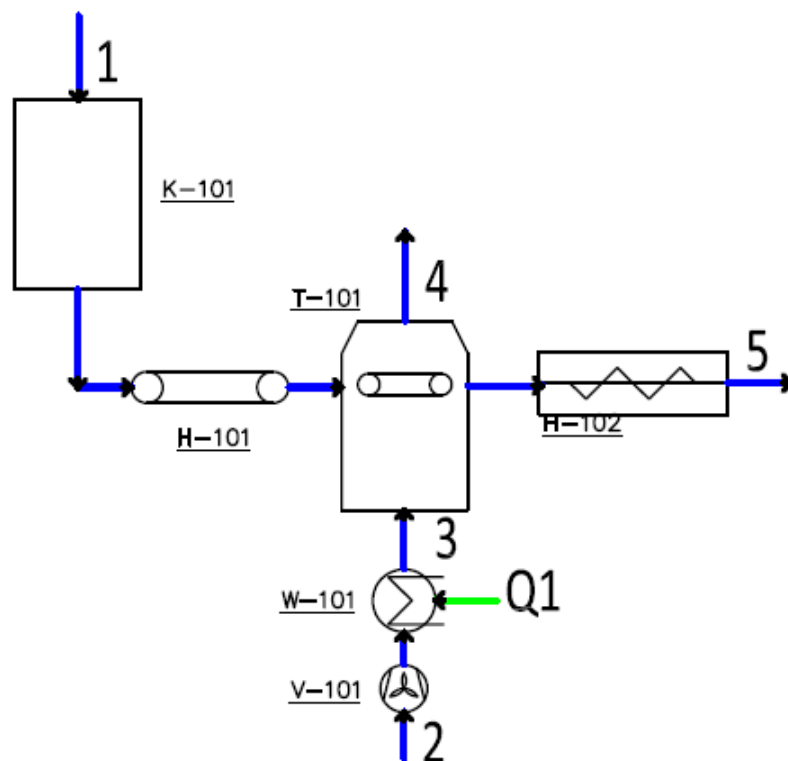


Figure 16: Drying section

4.2.2 Pyrolysis section

This section consists of pyrolysis reactor *K-201* with two input streams – *stream 5* composing of wood chips after drying process and *stream 15* composing of heated sand that serves as heat carrier inside the rotating cone pyrolysis reactor (see Chapter 3.4.4). After pyrolysis reaction takes place, *stream 6* composing of sand, char, gas and unreacted biomass leads to a battery of cyclone separators represented as *F-201* and *F-202*, followed by electrostatic separator *F-203*. Both cyclone separators *F-201* and *F-202* are expected to have 85 % efficiency. Remaining particles shall be separated in electrostatic separator *F-203*. All solid particles are then gathered up in vessel *K-202* and transported via screw conveyor *H-201* in *stream 13*. Gaseous product is transported thanks to induced draft fan *V-201* into *stream 11* with safety gas flare *A-201*. The scheme can be seen in Figure 17.

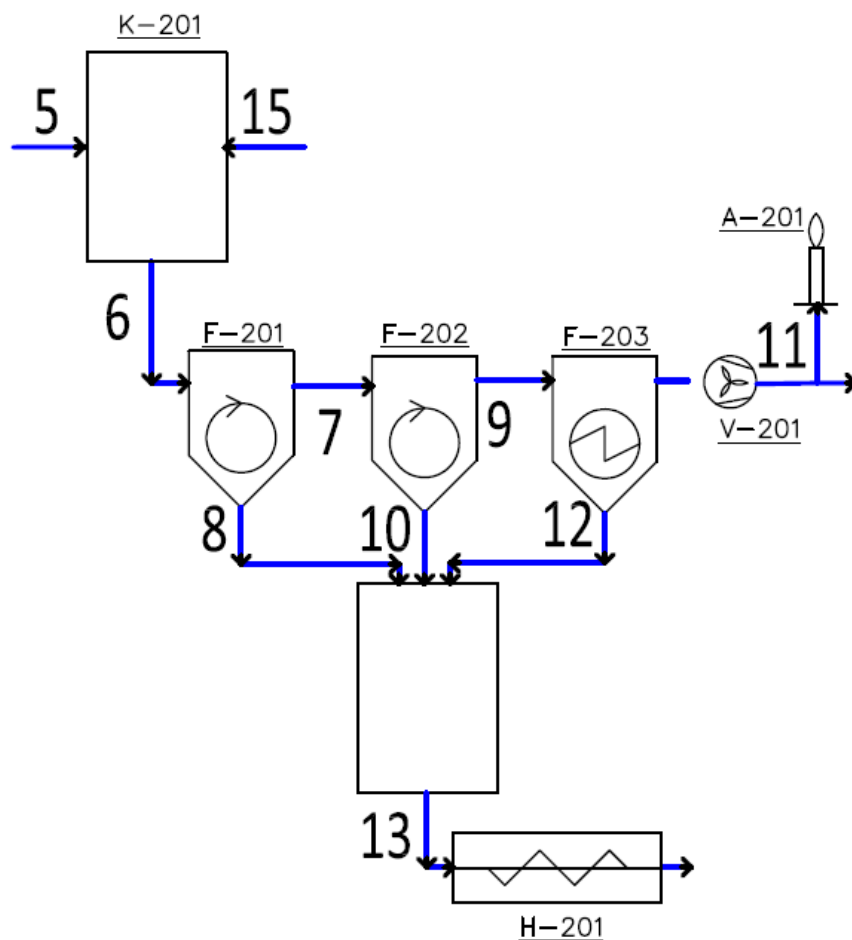


Figure 17: Pyrolysis section

4.2.3 Oil section

Pyrolysis gas free of solid particles is introduced to condenser *K-301*, where the condensable portion is transformed to pyrolysis oil thanks to being sprayed by a stream of already condensed oil through nozzles *A-301*. Condensed oil is pumped by pump *P-301* and is cooled in heat exchanger *W-301*, resulting in *stream 21*. This stream is further divided in two, *stream 23* is deposited in tank *K-302* as the primary product of pyrolysis and *stream 22* is forced back to the condenser where it quenches pyrolysis gas and causes its condensation. Incondensable gases leave condenser in *stream 24*. The described scheme can be seen in Figure 18.

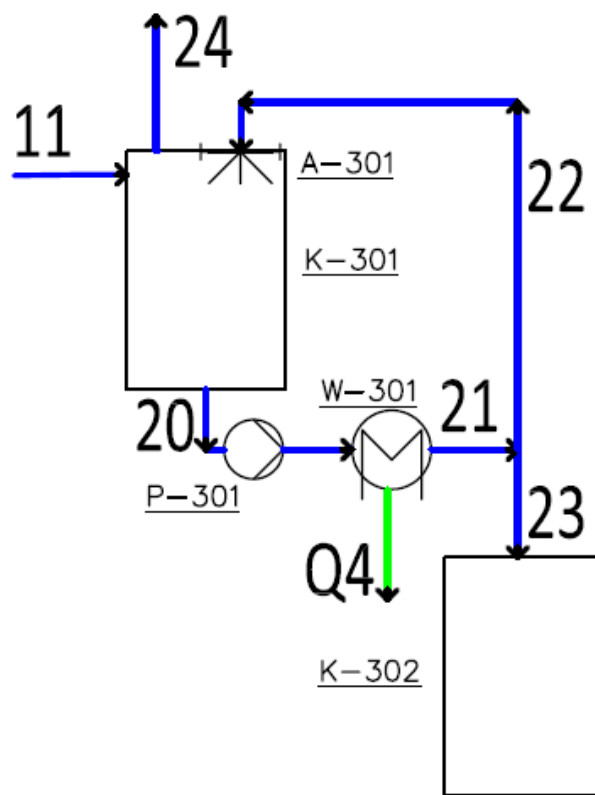


Figure 18: Oil section

4.2.4 Combustion section

The final part of technology is the combustion section. Pyrolysis gases from the oil section are induced by fan *V-401* inside combustion chamber represented as *D-401*. Char, unprocessed biomass and sand are also transported inside the combustor in *stream 13*. Char, pyrolysis gases and remaining biomass are burned with the addition of air, that is driven inside in *stream 25* via fan *V-402*. This results in generating heat that raises the temperature of the sand medium. Sand is then transported via screw conveyor *H-401* in *stream 14*, going through heat exchanger *W-401* that serves to regulate the temperature of the sand, therefore regulate the temperature in pyrolysis reactor and control the reaction. Flue gas and ash that remain after burnout in combustion chamber leave in *stream 16* and ash is removed in cyclone separator *F-401*. The flue gas then passes through heat exchanger *W-402* that recuperates excess heat in *energy stream Q3* and utilizes it for *energy stream Q1*, thus heating air that enters dryer *T-101*. The scheme is shown in Figure 19.

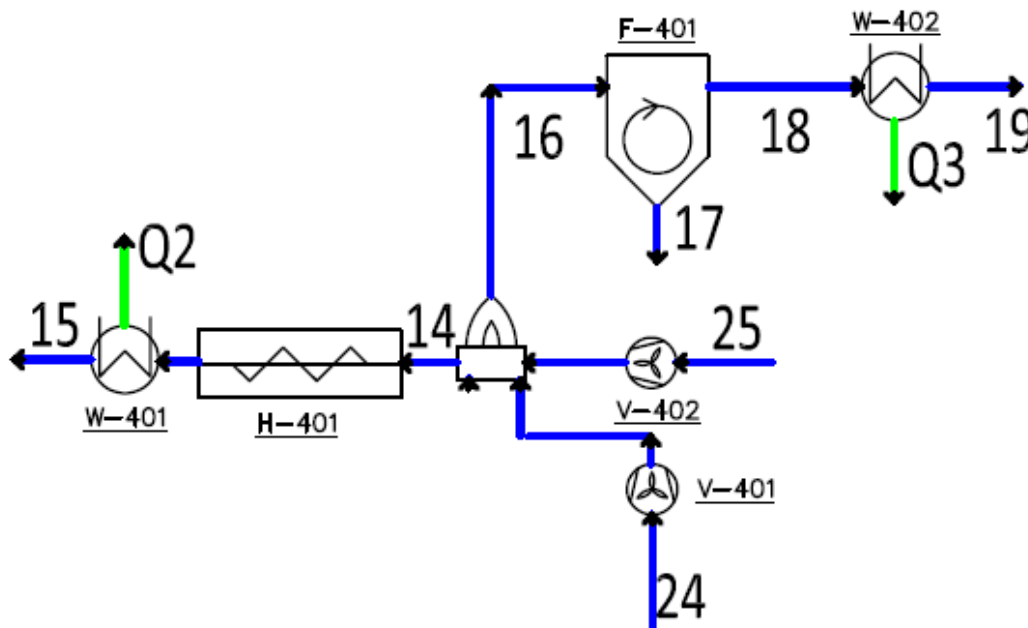


Figure 19: Combustion section

4.3 Model setup

Several assumptions were made during model creation, namely:

- Law of energy and material conservation.
- No heat losses towards the surrounding are expected.
- The efficiency of all process units is 100 %, if not specified otherwise.
- The process that takes part in one specific process unit is assumed to be isothermal.
- Mass and temperature are equally distributed over the interior of process units.
- Ventilators cause sufficient pressure difference to cover pressure drops in process units and to ensure a desirable flow of gases.
- Combustion is expected to be complete.
- Whole process and units are calculated in steady-state with no mass or energy accumulation in process units after facility start-up took place.

Several process parameters were assumed, most important ones:

- Input flow of biomass at 40 wt. % moisture is 1000 kg/h,
- All compounds taken from the surrounding, such as air or biomass input have a temperature of 20 °C,
- The temperature of the air entering dryer is 80 °C, to minimize the risk of biomass decomposition before entering the reactor.
- Estimation of biomass temperature increase at dryer outlet is 0 °C to ensure that even the worst possible outcome will still fulfill proposed balance calculations. Laboratory or pilot plant measurement is recommended to estimate this value.
- So-called water compound represents excess water that is supposed to evaporate from entering biomass at 40 wt. % down to 5 wt. % moisture.
- Water from remaining moisture content of 5 wt. % is evaporated in pyrolysis reactor and is expected to become a part of pyrolysis oil, therefore water as the alone standing compound is no longer part of any stream after pyrolysis reaction.
- The temperature of pyrolysis is 480 °C.
- Previously covered model of primary and secondary cracking (see Chapter 3.1.2) is used to describe the reaction itself with constants taken from [38], [39], [32].

- Designed reaction time is 2.5 seconds and composition at that very moment can be seen in Figure 20, namely 98 kg/h of unreacted biomass, 44 kg/h of char, 166 kg/h of non-condensable gases and 341 kg/h of condensable gases.
- The temperature of combustion is 850 °C, resolving in even temperature of combustion products – ash, hot sand, flue gas.
- Energy gained from combustion is determined by the lower heating value of the material.
- The temperature of flue gas at the outlet can be decreased down to 20 °C, flue gas is released into ambient with no cleaning requirement. Additionally, electrostatic separator or fabric filter might be used if necessary [67].
- The temperature of oil condensation is taken as 60 °C.

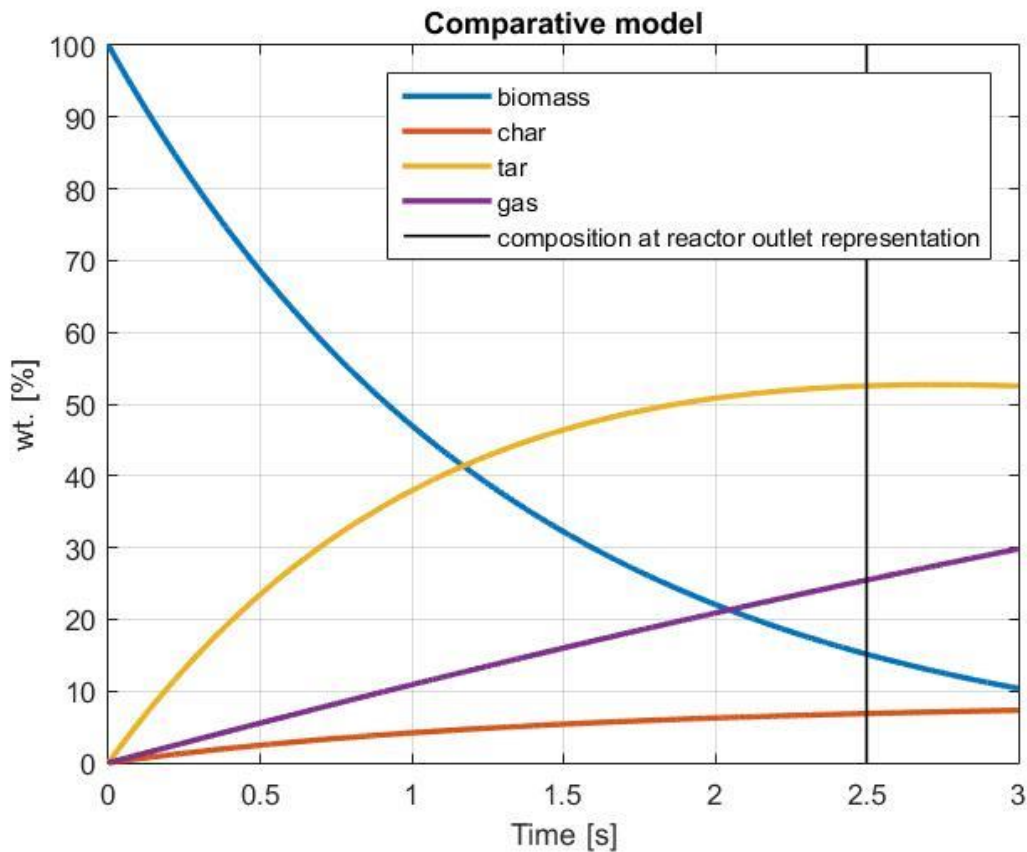


Figure 20: Reaction process

4.4 Process units balance calculations

This chapter shows the author's approach to balance the most important units. All these calculations were implemented into MATLAB and can be seen in Annex 1. The author would like to note, that values of mass and energy flow that can be seen in the process flow diagram in Annex 3 are taken over from the MATLAB environment. Due to this fact, the values proposed in the following lines might slightly differ.

4.4.1 Dryer T-101

Input to the dryer is wood at the mass flow of 1000 kg/h and 40 wt. % moisture with a desire to remove water down to 5 wt. % moisture. Therefore, the mass flow of water to be removed is:

$$m_W = m_{BFEEED} \cdot (w_{IN} - w_{OUT}), \quad (4)$$

$$m_W = 1000 \cdot (0.4 - 0.05) = 350 \frac{kg}{hour}. \quad (5)$$

Three states of air must be determined, representing ambient air, air after temperature increase and air at the end of the drying process.

Ambient air is expected to be 20 °C with a relative humidity of 70 % (see point 1 in Figure 21). In the Mollier diagram can be seen, that this state of air is represented by the moisture content of 10.5 g/kg and specific enthalpy of 46 kJ/kg.

Air after passing through heat exchanger *W-101* is represented by the second state (see point 2 in Figure 21). Heating between state 1 and state 2 occurs at constant moisture content. The second state is therefore given by temperature 80 °C and specific enthalpy of 108 kJ/kg.

Removing of moisture from wood to air occurs at constant enthalpy and is given by designed relative humidity of 70 % at outlet. The third state of air is therefore identified by the moisture content of 27.5 g/kg (see point 3 in Figure 21).

How much water can be removed by 1 kg/h of air between states 2 and 3 is calculated:

$$m_{1W} = x_3 - x_2, \quad (6)$$

$$m_{1W} = 0.0275 - 0.0105 = \mathbf{0.017 \frac{kg}{hour}}. \quad (7)$$

The mass flow of necessary air for the dryer can be calculated thanks to the knowledge of how much water needs to be removed and how much water does 1 kg/h of air remove:

$$m_A = \frac{m_W}{m_{1W}}, \quad (8)$$

$$m_A = \frac{350}{0.017} = \mathbf{20590 \frac{kg}{hour}}. \quad (9)$$

Heat duty required to heat this amount of air from state 1 to state 2 is calculated:

$$Q_{DRYER} = m_{AIR} \cdot (h_2 - h_1), \quad (10)$$

$$Q_{DRYER} = \frac{20590}{3600} \cdot (108 - 46) = \mathbf{354 kW}. \quad (11)$$

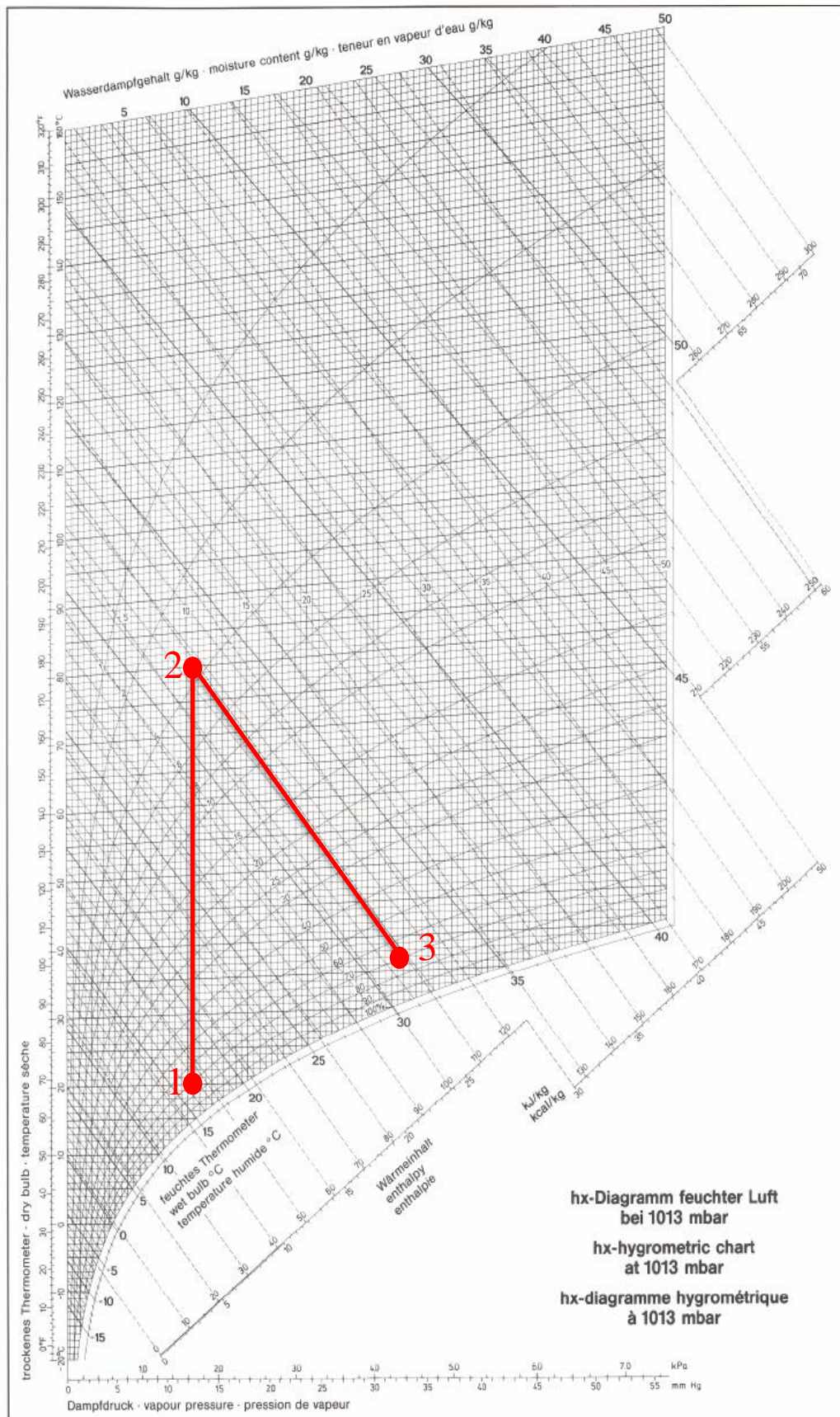


Figure 21: Mollier chart for dryer T-101 [68]

4.4.2 Condenser K-301

Gases from pyrolysis reactor are introduced to condenser *K-301* at temperature 480 °C and rate 507 kg/h, out of which 166 kg/h are non-condensable pyrolysis gases and 341 kg/h are gases condensable that form pyrolysis oil compound. The expected temperature of pyrolysis oil condensation is 60 °C [13], [21] and to ensure condensation of gas, approx. 840 kJ/kg of latent heat must be removed [69], [70] and gas specific heat capacity is suggested 1.1 kJ/(kg·K) [71]. After condensation at condensation temperature, oil is pumped through the heat exchanger *W-301* to cool down to from 60 °C to 20 °C. A portion of already condensed oil ensuring condensation of upcoming pyrolysis gases is pumped back to the system and sprayed from the top of the quencher. The remaining oil is stored as a product.

First of all, the amount of heat necessary to be removed for gas cooling and oil condensation is calculated:

$$Q_{COND} = (m_L + m_G) \cdot c_{PG} \cdot (T_{REAC} - T_{COND}) + m_L \cdot h_L, \quad (12)$$

$$Q_{COND} = \frac{(341 + 166)}{3600} \cdot 1.1 \cdot (480 - 60) + \frac{341}{3600} \cdot 840 = 144 \text{ kW}. \quad (13)$$

The amount of circulating oil, necessary for gas condensation (assuming it has temperature 20 °C after being cooled and temperature might rise up to 60 °C) is calculated. Assumed oil specific heat capacity is 2.5 kJ/(kg·K) [71].

$$m_{CIRC} = \frac{Q_{COND}}{c_L \cdot (T_{COND} - T_{LCOOL})}, \quad (14)$$

$$m_{CIRC} = \frac{144}{2.5 \cdot (60 - 20)} \cdot 3600 = 5184 \frac{\text{kg}}{\text{hour}}. \quad (15)$$

For sake of good order, the heat duty of heat exchanger *W-301* that cools all condensed oil from 60 °C to 20 °C is calculated:

$$Q_{COOL} = (m_L + m_{CIRC}) \cdot c_L \cdot (T_{COND} - T_{LCOOL}), \quad (16)$$

$$Q_{COOL} = \frac{(341 + 5184)}{3600} \cdot 2.5 \cdot (60 - 20) = 153 \text{ kW}. \quad (17)$$

4.4.3 Combustion chamber D-401

Firstly, the amount of energy that can be acquired thanks to the combustion of unreacted biomass, char and pyrolysis gas is calculated. The reported lower heating value of wood biomass is 15.6 MJ/kg [72], char is 27.5 MJ/kg [73] and gas is 9.5 MJ/Nm³ at 101325 Pa and 273 K [74].

Table 4: Example of pyrolysis gas composition [13]

Compound	Mole percent [%]	Molar mass [kg/kmol]
Methane CH ₄	8	16.04
Carbon dioxide CO ₂	20	44.01
Carbon monoxide CO	20	28.01
Hydrogen H ₂	38	2.02
Nitrogen N ₂	14	28
Pyrolysis gas	100	20.4

The first step is to transpose the undesirable unit of gas heating value. The equation of state to transfer mass flow of gas into volume flow at given conditions can be used. The molar mass of gas is taken from a usual pyrolysis gas composition as 20.4 kg/kmol (see Table 4).

$$V_G = \frac{m_G \cdot R \cdot T}{p \cdot M_G}, \quad (18)$$

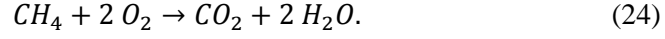
$$V_G = \frac{166 \cdot 8.314 \cdot 273}{101.325 \cdot 20.4} = 182 \frac{m^3}{hod} \quad (19)$$

Heat power gained from combustion is given as:

$$Q_{COMB} = m_B \cdot LHV_B + m_C \cdot LHV_C + V_G \cdot LHV_G, \quad (20)$$

$$Q_{COMB} = \frac{98}{3600} \cdot 15.6 \cdot 1000 + \frac{44}{3600} \cdot 27.5 \cdot 1000 + \frac{182}{3600} \cdot 9.5 \cdot 1000 = 1241 \text{ kW}. \quad (21)$$

Amount of air necessary for combustion is calculated, assuming 1.5 oxygen excess ratio compared to pyrolysis gas molar flow [72] and air-fuel mass flow ratio for biomass and char combustion as 6 [73]. Firstly, equations that describe the combustion of non-inert pyrolysis gas compounds are written:



The amount of oxygen required for pyrolysis gas combustion with the desired excess ratio is calculated:

$$n_{O_2} = \lambda_G \cdot (c_{CO}^n \cdot 0.5 + c_{H_2}^n \cdot 0.5 + c_{CH_4}^n \cdot 2) \cdot \frac{m_G}{M_G}, \quad (25)$$

$$n_{O_2} = 1.5 \cdot (0.2 \cdot 0.5 + 0.38 \cdot 0.5 + 0.08 \cdot 2) \cdot \frac{166}{20.4} = 5.5 \frac{kmol}{h}. \quad (26)$$

Thanks to it, the mass flow of required air is calculated, assuming its molar mass as 29kg/kmol [75]:

$$m_{AIR} = \frac{n_{O_2}}{c_{O_2AIR}^n} \cdot M_{AIR} + \lambda_C \cdot m_C + \lambda_B \cdot m_B, \quad (27)$$

$$m_{AIR} = \frac{5.5}{0.21} \cdot 29 + 6 \cdot 44 + 6 \cdot 98 = 1611 \frac{kg}{hour}. \quad (28)$$

According to [76], [77], 4 % of biomass after combustion turns into ash and 7 % of char turns into ash after combustion, according to [78]. Therefore, the amount of ash can be calculated:

$$m_{ASH} = m_C \cdot c_{ASHC}^m + m_B \cdot c_{ASHB}^m, \quad (29)$$

$$m_{ASH} = 44 \cdot 0.07 + 98 \cdot 0.04 = 7 \frac{kg}{hour}. \quad (30)$$

Applying mass conservation law to the combustion chamber with unreacted biomass, char, sand, pyrolysis gas, and air as input and sand, ash and flue gas as output can determine the amount of flue gas leaving the combustion chamber:

$$m_{FLUEGAS} = m_{AIR} + m_B + m_C + m_G - m_{ASH}, \quad (31)$$

$$m_{FLUEGAS} = 1611 + 98 + 44 + 182 - 7 = 1928 \frac{kg}{hour}. \quad (32)$$

Heat duty required to heat inputs up to combustion temperature from corresponding temperature of the material before entering the combustion chamber is calculated. Air is assumed with a mean specific heat capacity of 1.06 kJ/(kg·K) [79]:

$$Q_{AIR} = m_{AIR} \cdot c_{PAIR} \cdot (T_{COMB} - T_{AMB}), \quad (33)$$

$$Q_{AIR} = \frac{1611}{3600} \cdot 1.06 \cdot (850 - 20) = \mathbf{394 \text{ kW}}. \quad (34)$$

Char is expected to have a mean specific heat capacity of 1.7 kJ/(kg·K), according to [80]:

$$Q_C = m_C \cdot c_C \cdot (T_{COMB} - T_{REAC}), \quad (35)$$

$$Q_C = \frac{44}{3600} \cdot 1.7 \cdot (850 - 480) = \mathbf{8 \text{ kW}}. \quad (36)$$

Gas with the specific heat capacity of 1.1 kJ/(kg·K), according to [71], is assumed:

$$Q_G = m_G \cdot c_G \cdot (T_{COMB} - T_{COND}), \quad (37)$$

$$Q_G = \frac{166}{3600} \cdot 1.1 \cdot (850 - 60) = \mathbf{40 \text{ kW}}. \quad (38)$$

Unreacted biomass is assumed to have a mean specific heat capacity of 3.7 kJ/(kg·K) [80]:

$$Q_B = m_B \cdot c_B \cdot (T_{COMB} - T_{REAC}), \quad (39)$$

$$Q_B = \frac{98}{3600} \cdot 3.7 \cdot (850 - 480) = \mathbf{37 \text{ kW}}. \quad (40)$$

Heat exchanger *W-402* serves to cool flue gas from combustion temperature down to the temperature of surrounding, utilizing this heat duty to heat air entering dryer *T-101*. Specific heat capacity of air is supposed to correlate with that of flue gas:

$$Q_{FLUEGAS} = m_{FLUEGAS} \cdot c_{PAIR} \cdot (T_{COMB} - T_{AMB}), \quad (41)$$

$$Q_{FLUEGAS} = \frac{1928}{3600} \cdot 1.06 \cdot (850 - 20) = \mathbf{470 \text{ kW}}. \quad (42)$$

In the combustion chamber, heat is generated by the combustion of unreacted biomass, char and pyrolysis gas. Some of the heat is utilized to heat inputs up to reaction temperature, some heat is removed by flue gas and remaining heat that is generated in the chamber must be removed by being transferred to circulating sand in order to ensure no accumulation of heat takes place. This determines the amount of circulating sand with its specific heat capacity of 0.83 kJ/(kg·K) [81]:

$$\mathbf{m}_{SAND} = \frac{Q_{COMB} - Q_C - Q_G - Q_B - Q_{AIR} - Q_{FLUEGAS}}{c_{SAND} \cdot (T_{COMB} - T_{REAC})}, \quad (43)$$

$$\mathbf{m}_{SAND} = \frac{1241 - 8 - 40 - 37 - 394 - 470}{0.83 \cdot (850 - 480)} = \mathbf{3456} \frac{\mathbf{kg}}{\mathbf{hour}}. \quad (44)$$

The complete diagram of the energy balance for the combustion chamber can be seen in Figure 22.

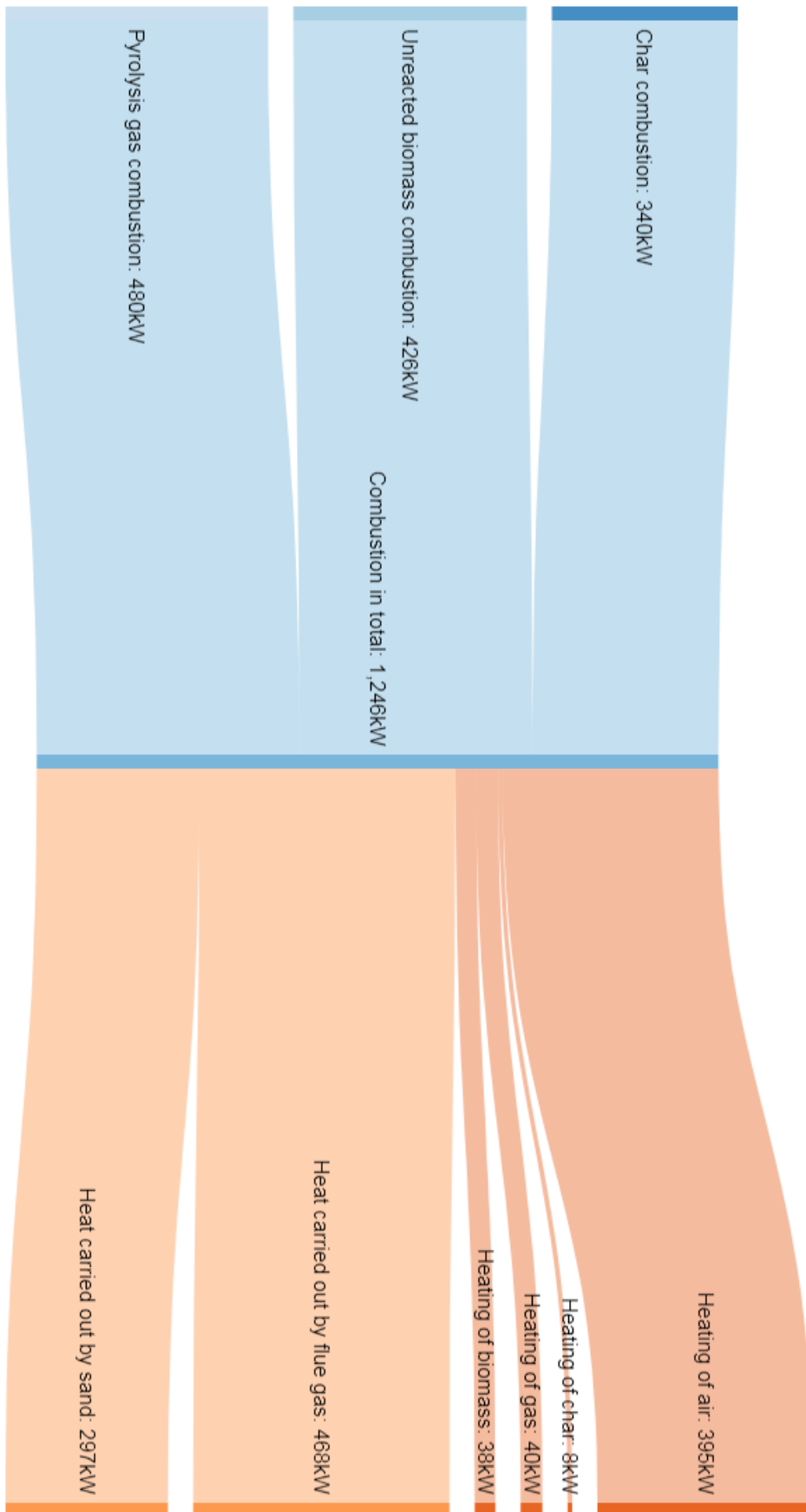


Figure 22: Sankey diagram for energy balance

4.4.4 Pyrolysis reactor K-201

Firstly, the amount of heat power required to be transferred from sand to biomass to drive the pyrolysis reaction is calculated. This energy consists of:

- The heat required to raise the temperature of dry biomass from 20 °C up to 480 °C.
- Latent heat of evaporation for the remaining portion of water to evaporate.
- Reaction enthalpy for that mass flow of biomass that was decomposed to pyrolysis products.

Specific heat capacity of biomass is taken as the mean between reaction and ambient temperatures from [80], a small portion of the remaining water in it is considered as negligible for specific heat capacity value. Latent heat of water evaporation is taken from [82] and reaction enthalpy for pyrolysis is estimated 400 kJ/kg from [83]:

$$Q_{REAC} = m_{BDRYER} \cdot c_B \cdot (T_{REAC} - T_{AMB}) + m_{BFEEED} \cdot w_{OUT} \cdot h_W + [m_{BDRYER} \cdot (1 - w_{OUT}) - m_B] \cdot h_{PYRO}^R \quad (45)$$

$$Q_{REAC} = \frac{650}{3600} \cdot 2.1 \cdot (480 - 20) + \frac{1000}{3600} \cdot 0.05 \cdot 2256 + \left[\frac{650}{3600} \cdot (1 - 0.05) - \frac{98}{3600} \right] \cdot 400 = \mathbf{263 \text{ kW}}. \quad (46)$$

4.4.5 Sand cooler W-401

Mass flow of sand that leaves the combustion chamber at 850 °C is utilized to transfer heat duty in the pyrolysis reactor. Input temperature of sand can be calculated from the knowledge of energy required to drive the reaction, further determining the heat duty of sand cooler that serves to control the reaction:

$$T_{SANDCOOL} = \frac{Q_{REAC}}{m_{SAND} \cdot c_{SAND}} + T_{REAC}, \quad (47)$$

$$T_{SANDCOOL} = \frac{263}{\frac{3456}{3600} \cdot 0.83} + 480 = \mathbf{810 \text{ }^\circ\text{C}}. \quad (48)$$

The heat duty of the heat exchanger *W-401* can be calculated:

$$Q_{SANDCOOL} = m_{SAND} \cdot c_{SAND} \cdot (T_{COMB} - T_{SANDCOOL}), \quad (49)$$

$$Q_{SANDCOOL} = \frac{3456}{3600} \cdot 0.83 \cdot (850 - 810) = \mathbf{32 \text{ kW}}. \quad (50)$$

4.5 Energy supply for pyrolysis reaction

As can be seen in Figure 14 which shows a scheme of reference technology to this model, there is no other fuel stream required to run the process and also excess heat is utilized to produce steam and electricity. This signalizes a major difference compared to other technologies stated in Chapter 3.5, that required external energy flow entering the pyrolysis reactor obtained e.g. by burning natural gas. This was confirmed by [21], as the process itself requires start-up of the facility by burning natural gas to heat circulating sand, afterward there is no further need to input any external energy, combustion of char, unreacted biomass and pyrolysis gas is sufficient to cover the required heat in pyrolysis reactor as well as the dryer. As reported in [84], EMPYRO facility in the Netherlands operates with wood moisture of 10-12 wt. %. From the author's point of view, this wood could be considered rather dry. It really depends on the available quality of wood chips feedstock, so the author assumed moisture of wood for this model of 40 wt. %. There are 4 external energy streams present in the process flow diagram with two biggest values of $Q1$ – the energy required to heat drying air and $Q3$ – the energy available in flue gas leaving the combustion chamber. As can be seen, there is no external energy stream required to run the reaction in the pyrolysis reactor. Additionally, calculated excess energy in flue gas stream $Q3$ is greater than required energy in stream $Q1$, therefore this technology with given process parameters and properties that are used in the model is self-driven. Once the process is started-up, e.g. by burning natural gas, it becomes self-sustainable and is only controlled by the plant operator. This calculation could be considered confirmed by the successful realization of reference technology [21].

4.6 Critical moisture

As the excess heat from combustion is taken out by flue gas, it could be used to heat air in the dryer that then removes excess water from wood chips, there must be a limiting critical moisture content of wood that indicates maximal wood moisture that still secures continuity of process without additional heat. A script that calculates this value of moisture can be seen in Annex 2. According to the author's results, this value should be approx. 47 wt. %. As reported in [63], the value proposed by reference technology is 55 wt. %, which indicates solidly corresponding value.

5 PYROLYSIS OIL ANALYSIS AND DISCUSSION

This chapter was developed thanks to cooperation with UniCRE, namely Ing. et Ing. Kateřina Svobodová and Ing. Jiří Hájek, MBA. A basic analysis of three pyrolysis oil samples from various feedstocks and their comparison is provided. There is a pyrolysis bio-oil from EMPYRO, the Netherlands; tires pyrolysis oil and plastics pyrolysis oil. Analysis and data from these samples that can be seen in Table 5 and Table 6 were provided by [85].

5.1 Pyrolysis oil analysis

Table 5 shows the chemical composition of pyrolysis bio-oil. Very high content to oxygen has to be taken into consideration because it indicates low energy density, corrosion propensity, might be the reason for chemical instability and causes poor miscibility with hydrocarbons [86], [48]. The water content was not measured, literature usually states 15-30 wt. %, leading to lowering the heating value. On the other hand, it also improves flow characteristics that are beneficial for pumping pyrolysis oil [86].

Table 6 shows the properties of previously mentioned pyrolysis oil samples, that might help during the eventual design of the oil section (see Chapter 4.2.3) and also to thoroughly consider oil storage and transportation. Relatively high-density value might indicate higher content of high-molecular matter (resin), lignin oligomers, etc. [85].

Bromine number indicates the contribution of unsaturated hydrocarbons in the sample and can be used as an indicator of chemical stability. Generally, from the industrial perspective, lower bromine number indicates that less hydrogen is required to transform unsaturated hydrocarbons into saturated ones in hydrotreating processes, while higher bromine number predicates the opposite [85], [87]. As can be seen in Table 6, pyrolysis bio-oil has lower bromine number than the other two samples from different feedstocks.

Energy density represented as the higher or lower heating value was not evaluated. Literature data show higher heating value varying from 15 up to 20 MJ/kg [41], [86]. According to the statistical approach by [88], [89], the value can be determined based on carbon, hydrogen and oxygen content. For the available analysis of pyrolysis bio-oil (see Table 5), this value was calculated as 17.4 MJ/kg, correlating with literature research. These values are approx. half the amount of fuel oil heating value which is usually up to 40 MJ/kg [86], [90].

In order to achieve the better composition of pyrolysis oil, therefore better properties and better possible utilization at refineries, use of catalysts during pyrolysis is suggested and overview can be found in [91].

Table 5: Pyrolysis bio-oil composition [85]

Element	Content
Carbon	44.9 wt. %
Hydrogen	6.69 wt. %
Nitrogen	717 mg/kg
Sulfur	24.5 mg/kg
Oxygen	48.33 wt. %
Chlorine	4.7 mg/kg
Calcium	13.7 mg/kg
Magnesium	4.56 mg/kg
Potassium	11.3 mg/kg
Lead	<0.2 mg/kg
Vanadium	<0.2 mg/kg
Iron	1.62 mg/kg
Sodium	2.74 mg/kg
Manganese	2.01 mg/kg

Table 6: Pyrolysis oil samples properties [85]

Parameter	Unit	Bio oil	Tires pyrolysis oil	Plastics pyrolysis oil
Density [15 °C]	kg/m ³	1217.98	862.97	773.03
Kin. viscosity [40 °C]	mm ² /s	37.35	1.23	1.44
Pour point	°C	-17	<-70	1
Bromine number	g Br/100 g	7.13	104.86	42.93

5.2 Pyrolysis oil application

One of the easily approachable ways to utilize pyrolysis oil is its combustion as fuel oil. This possibility is already applied in the industry as can be seen in Chapter 2.2.2, where actual trends are described, as well as in literature resources [86], [48]. Bio-oil can be combusted e.g. in diesel engines or turbines. However, a slight modification might be required to balance previously described properties or compounds of pyrolysis oil that differ from typical fuel oils [21]. From the author's point of view, this application might be the most easily applicable, however, this requires a transformation of biomass into fuel by pyrolysis unit. Better storage, transportation, and energy density might differ compared to raw biomass. Potentially, a small pyrolysis unit might be placed at agriculture area, utilizing its residues with pyrolysis and selling the produced oil.

Another potential of pyrolysis oil might be in technologies processing petroleum residues. Fluid catalytic cracking that transforms high-molecular substances into other desirable products might be suitable [9]. It was found by [61], [92], that around 5-10 wt. % of pyrolysis oil may be added to feed of fluid catalytic cracking, resulting in little or no impact on product yield and quality. Thermal cracking in a heated furnace (visbreaking or coking) might also be considered [93], [85]. Hydrocracking, which combines the cracking of larger molecules and hydrogenation at the same time could also be used [9], [85]. In addition to the desired lighter products, there is a potential to obtain a solid product for fertilizers production or quality coke with good sorption properties or carbon black for the rubber industry. Nevertheless, additional research is necessary [85].

In order to utilize pyrolysis oil in previously described refinery processes in the future, some technological improvements are suggested. Namely, partial condensation of primary product gas that would lead to receiving desired pyrolysis oil fractions such as gasoline fraction (up to approx. 180 °C), diesel fraction (up to approx. 360 °C) and the heavy residue. Utilization and processing of these fractions would be then more feasible on existing refinery hydrotreating units for fuel production, for example in the form of co-processing with standard crude oil feedstock. Hydrotreating consists of several processes. Undesirable oxygen contained in the bio-oil feed is removed in the form of water via hydrodeoxygenation, similarly sulfur and nitrogen in hydrodesulphuration and hydrodenitrogenation processes, respectively. Concurrently hydrogenation of unsaturated hydrocarbons takes place. The hydrogen consumption varies and is closely related to oxygen, sulfur, nitrogen and total unsaturated hydrocarbons content in the feedstock [85].

Generally, the analysed sample of bio-oil contained a small amount of unsaturated hydrocarbons (low bromine number) as well as sulfur, most of the hydrogen would be then consumed for hydrodeoxygenation. Thanks to the process of hydrodeoxygenation, unwanted oxygen would be excluded in the form of water. Hydrogenating processes would then transform unsaturated hydrocarbons into saturated ones. Hydrogen consumption for this process is the smaller the lower bromine number is [85]. Heavy residues, that could be contained up to 50 wt. % in bio-oil depending on its origin would be possibly further utilized in one of the previously described technologies for heavy residues processing or used as fuel oil depending on their composition and properties [85].

The aromatics content was not analytically measured. Available liquid chromatography method could not have been applied, the sample of bio-oil was not soluble in the used solvent (n-heptane). Nevertheless, literature sources suggest the content of aromatic and other valuable compounds which could be recovered for further utilization in the petrochemical industry [48], [86].

SimDist distillation curve of pyrolysis oil samples can be seen in Figure 23. Simulated distillation is a fast gas chromatography method used to characterize petroleum fractions and products since it permits the quick determination of their boiling range distribution. Sample preparation for this analysis consists of dissolution in carbon disulfide. The bio-oil sample was not completely soluble in this solvent, therefore the SimDist was provided only for the dissolved minor part of the sample.

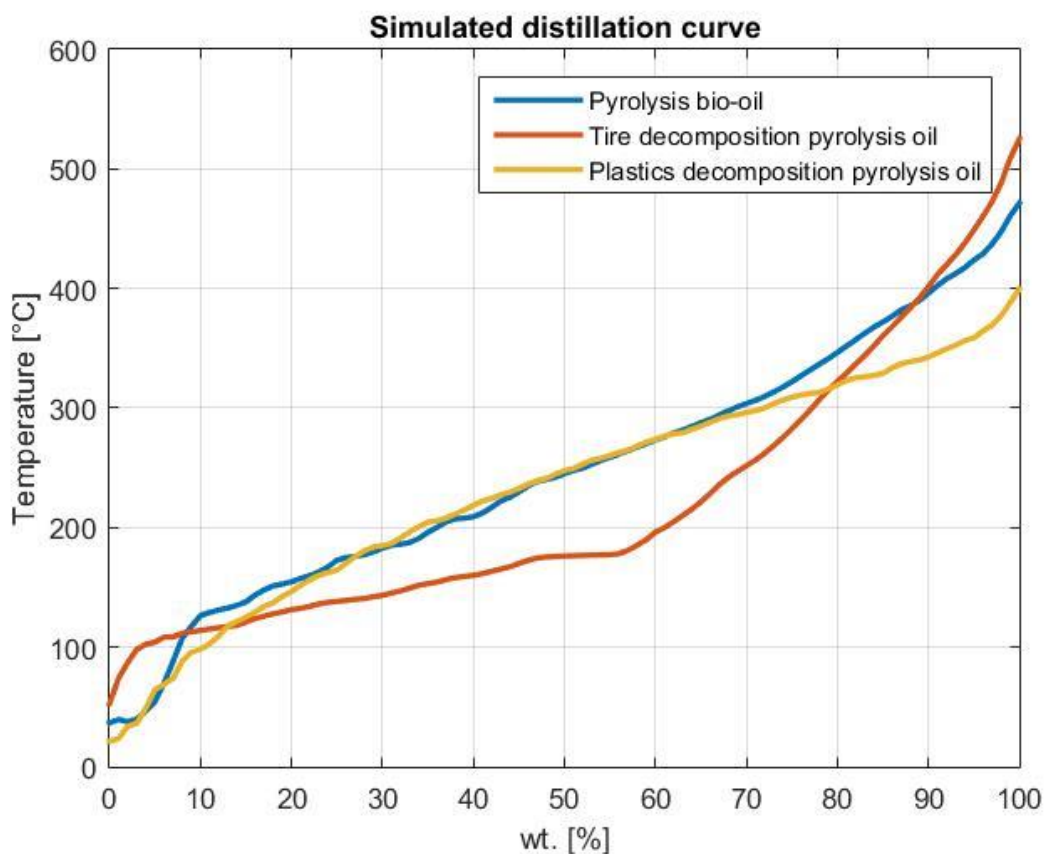


Figure 23: Simulated distillation curve

6 CONCLUSION

The thesis provides a summary of waste management, mainly of biomass waste. Several treatment possibilities are listed and thermochemical conversion methods are further analyzed with a focus on pyrolysis. Research of currently running pyrolysis plants in worldwide scale is noted. Pyrolysis is described in terms of process conditions, the suitability of various materials as feedstock, models describing material decomposition and utilization of its products.

In literature, industrial and patent research, several variations of pyrolysis reactors are listed and further analyzed from plant operator's point of view and the current trends in pyrolysis topic. Based on these reactors, a few schemes that were proven suitable for pilot or industrial scale pyrolysis are described.

The main part of this thesis is the creation of process flow diagram and appropriate mass and energy balance calculations. Data provided by the plant operator as well as data found in the literature were used with an emphasis on easy modifications of the model if certain values need to be clarified or changed. Process flow diagram provides a list of process units, components streams with designed temperature and mass flow and external energy flows.

Next, the process of pyrolysis is checked in terms of energy requirement and confirmed as possible to run the plant in steady continuous mode after start-up without external energy sources, depending on by-product utilization in terms of providing fuel to drive the process and critical moisture of biomass that is determined by the quality of the feedstock.

Lastly, the pyrolysis oil utilization was discussed. It turns out, that at this very moment, the best solution appears to use it as fuel oil, because of its undesirable composition, mainly content of oxygen and high-molecular compounds. These could cause technological problems at existing oil refineries. In order to improve pyrolysis oil processing, some upgrade possibilities were noted, mainly fluid catalytic cracking or partial condensation that would separate lighter fractions from those heavy fuel oil ones.

REFERENCES

1. KAZA, Silpa. What a waste 2.0: a global snapshot of solid waste management to 2050. Washington, DC: World Bank Group, [2018]. ISBN 978-146-4813-290.
2. World Bank (2012) What A Waste; A Global Review of Solid Waste Management. Urban Development Series, Knowledge Papers. Available at: <http://go.worldbank.org/BCQEP0TMO0> (accessed 22 June 2012).
3. Eurostat (2019-05-23) Municipal waste by waste management operations [Data file] Retrieved from http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_wasmun&lang=en
4. Eurostat (2019-04-02) Generation of waste by waste category, hazardousness and NACE Rev. 2 activity [Data file] Retrieved from http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=env_wasgen&lang=en
5. Eurostat (2019-04-02) Management of waste excluding major mineral waste, by waste management operations [Data file] Retrieved from <https://ec.europa.eu/eurostat/web/waste/management-of-waste-excluding-major-mineral-wastes>
6. Landfill. Cambridge Dictionary [online]. Cambridge University: Cambridge University Press, c2019 [cit. 2019-05-12]. Available at: <https://dictionary.cambridge.org/dictionary/english/landfill>
7. GUTIERREZ, D.M. Landfills Vs. Incinerators. Sciencing [online]. Santa Monica, USA: Leaf Group, c2019, April 24, 2017 [cit. 2019-05-10]. Available at: <https://sciencing.com/landfills-vs-incinerators-5523826.html>
8. Review of Waste Policy and Legislation. European Commission [online]. Brussels, Belgium: European Commission, c2019 [cit. 2019-05-06]. Available at: https://ec.europa.eu/environment/waste/target_review.htm
9. ŠULC, Radek. Průmyslová chemie. CTU in Prague, Faculty of Mechanical Engineering, Dpt. of Process Engineering, 2019. Available at: <https://moodle-vyuka.cvut.cz/course/view.php?id=969>
10. GEYER, R., J. R. JAMBECK a K. L. LAW. FAQs on Plastics. Our World In Data [online]. Oxford: University of Oxford, 2019 [cit. 2019-04-24]. Available at: <https://ourworldindata.org/faq-on-plastics#how-much-of-global-plastic-is-recycled>

11. Industrial Composting: What It Is and How It Works. UrthPath [online]. Lincoln, USA: UrthPath, c2019, August 24, 2017 [cit. 2019-07-30]. Available at:
<https://www.urthpact.com/industrial-composting-what-it-is-and-how-it-works/>
12. BASU, Prabir. Biomass gasification and pyrolysis: practical design and theory. Amsterdam: Elsevier, c2010. ISBN 978-0-12-374988-8.
13. BRIDGWATER, A. V. a G. GRASSI. Biomass pyrolysis liquids: upgrading and utilisation. New York, NY, USA: Sole distributor in the USA and Canada, Elsevier Science Pub., c1991. ISBN 18-516-6565-X.
14. Biomass Gasifiers. Infinite Energy Pvt. Ltd. [online]. Barakhamba Road, India: Infinite Energy Pvt, 2011 [cit. 2019-04-30]. Available at:
<http://www.infiniteenergyindia.com/biomass-gasifiers.html>
15. GOFF, Steve a Marco CASTALDI. Turning trash into renewable energy treasure. <https://www.slideshare.net/> [online]. Sunnyvale, USA: LinkedIn Corporation, c2019 [cit. 2019-05-15]. Available at:
<https://www.slideshare.net/mnetarwala/master-wtewebinarpresentation52413>
16. History and current state of Pyrolysis. Magnum Group International Inc. [online]. Vancouver, Canada: Magnum Group International, 2019 [cit. 2019-05-02]. Available at:
http://www.magnumgroup.org/images/History_and_current_state_of_Pyrolysis.pdf
17. KOZLO, A., B. TAMBUYSER, H. HEERES a B. VAN DE BELD. Chemical composition of ten biomass feedstocks and their suitability for conversion by fast pyrolysis. *Bio4Products*. 2019, 2019(1.), 1-24. DOI: 10.5281/zenodo.3275255.
18. WILLIAMS, Paul T. Pyrolysis of waste tyres: A review. *Waste Management*. 2013, 33(8), 1714-1728. DOI: 10.1016/j.wasman.2013.05.003. ISSN 0956053X. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0956053X13002122>
19. SCHEIRS, John a W. KAMINSKY. Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels. Hoboken, NJ: J. Wiley, c2006. ISBN 978-0-470-02152-1.
20. GRAUSE, Guido, Alfons BUEKENS, Yusaku SAKATA, Akitsugu OKUWAKI a Toshiaki YOSHIOKA. Feedstock recycling of waste polymeric material. *Journal of Material Cycles and Waste Management*. 2011, 13(4), 265-282. DOI: 10.1007/s10163-011-0031-z. ISSN 1438-4957. Available at:
<http://link.springer.com/10.1007/s10163-011-0031-z>

21. MUGGEN, Gerhard, Managing director at BTG-BTL [Business meeting]. Enschede, 2019-02-05
22. BTG Projects. BTG-BTL [online]. Enschede: BTG Biomass Technology Group, c2019 [cit. 2019-05-16]. Available at: <https://www.btg-btl.com/en/company/projects>
23. Joensuu CHP plant. Fortum [online]. Espoo, Finland: Fortum, 2019 [cit. 2019-67-12]. Available at: <https://www.fortum.com/about-us/our-company/our-energy-production/our-power-plants/joensuu-chp-plant>
24. Ontario facility. Ensyn [online]. Ottawa, Canada: Ensyn, c2015 [cit. 2019-06-08]. Available at: <http://www.ensyn.com/ontario.html>
25. SHI, Xiaogang, Frederik RONSSE a Jan G. PIETERS. Finite element modeling of intraparticle heterogeneous tar conversion during pyrolysis of woody biomass particles. *Fuel Processing Technology*. 2016, 148, 302-316. DOI: 10.1016/j.fuproc.2016.03.010. ISSN 03783820. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S037838201630114X>
26. *Fire Safety Journal*. 2007, 42(3). ISSN 03797112. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0379711206001263>
27. THURNER, Franz a Uzi MANN. Kinetic investigation of wood pyrolysis. *Ind. Eng. Chem. Proc. Des. Dev.* 1981, 20(3), 482-488. DOI: 10.1021/i200014a015. ISSN 0196-4305. Available at: <http://pubs.acs.org/doi/abs/10.1021/i200014a015>
28. PRAKASH, N. a T. KARUNANITHI. Kinetic Modeling in Biomass Pyrolysis – A Review. *Journal of Applied Sciences Research*. 2008, 4(12), 1627-1636.
29. SHAFIZADEH, F., COCHRAN, T. G., and SAKAI, Y., "Application of Pyrolytic Methods for the Saccharification of Cellulose", *AIChE Symposium Series* 184, Volume 75, 24 (1 979).
30. THURNER, Franz, Uzi MANN a Steven R. BECK. Kinetic investigation of wood pyrolysis. Texas Tech University, Lubbock, USA, 1980. Available at: <https://www.osti.gov/servlets/purl/6809951>
31. BROIDO, A., EVETT., M., HODGES, C.C., *Carbohydr. Res.* 44 (1975) 267-274
32. LIDEN, A.G., F. BERRUTI a D.S. SCOTT. A KINETIC MODEL FOR THE PRODUCTION OF LIQUIDS FROM THE FLASH PYROLYSIS OF BIOMASS. *Chemical Engineering Communications*. 2010, 65(1), 207-221. DOI: 10.1080/00986448808940254. ISSN 0098-6445. Available at: <https://www.tandfonline.com/doi/full/10.1080/00986448808940254>

33. KOUFOPANOS, C. A., A. LUCCHESI a G. MASCHIO. Kinetic modelling of the pyrolysis of biomass and biomass components. *The Canadian Journal of Chemical Engineering*. 1989, 67(1), 75-84. DOI: 10.1002/cjce.5450670111. ISSN 00084034. Available at: <http://doi.wiley.com/10.1002/cjce.5450670111>
34. SRIVASTAVA, V.K. a R.K. JALAN. Predictions of concentration in the pyrolysis of biomass materials—I. *Energy Conversion and Management*. 1994, 35(12), 1031-1040. DOI: 10.1016/0196-8904(94)90007-8. ISSN 01968904. Available at: <https://linkinghub.elsevier.com/retrieve/pii/0196890494900078>
35. GRIOUI, Najla, Kamel HALOUANI, André ZOULALIAN a Foued HALOUANI. Thermogravimetric analysis and kinetics modeling of isothermal carbonization of olive wood in inert atmosphere. *Thermochimica Acta*. 2006, 440(1), 23-30. DOI: 10.1016/j.tca.2005.09.018. ISSN 00406031. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0040603105005009>
36. DITL, Pavel. *Chemické reaktory*. Vyd. 3. V Praze: Nakladatelství ČVUT, 2006. ISBN 80-01-03576-X.
37. PARK, Won Chan, Arvind ATREYA a Howard R. BAUM. Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. *Combustion and Flame*. 2010, 157(3), 481-494. DOI: 10.1016/j.combustflame.2009.10.006. ISSN 00102180. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0010218009002843>
38. BLASI, Colomba Di a Carmen BRANCA. Kinetics of Primary Product Formation from Wood Pyrolysis. 2001, 40(23), 5547-5556. DOI: 10.1021/ie000997e. ISSN 0888-5885. Available at: <https://pubs.acs.org/doi/10.1021/ie000997e>
39. BLASI, Colomba Di. Analysis of Convection and Secondary Reaction Effects Within Porous Solid Fuels Undergoing Pyrolysis. *Combustion Science and Technology*. 1993, 90(5), 315-340. DOI: 10.1080/00102209308907620. ISSN 0010-2202. Available at: <http://www.tandfonline.com/doi/abs/10.1080/00102209308907620>
40. GUIZANI, Chamseddine, Mejdi JEGUIRIM, Sylvie VALIN, Lionel LIMOUSY a Sylvain SALVADOR. Biomass Chars: The Effects of Pyrolysis Conditions on Their Morphology, Structure, Chemical Properties and Reactivity. *Energies*. 2017, 10(6). DOI: 10.3390/en10060796. ISSN 1996-1073. Available at: <http://www.mdpi.com/1996-1073/10/6/796>

41. BROWNSORT, Peter Alexander. Biomass pyrolysis processes: Performance parameters and their influence on biochar system benefits. University of Edinburgh, 2009. Dissertation thesis. University of Edinburgh.
42. GHEORGHE, Cora Bulmău, Cosmin MĂRCULESCU, Adrian BADEA a Tiberiu APOSTOL. Pyrolysis parameters influencing the bio-char generation from wooden biomass. UPB Scientific Bulletin: Series C. 2010, 72(1), 29-38. ISSN 1454-234x.
43. JAHIRUL, Mohammad, Mohammad RASUL, Ashfaque CHOWDHURY a Nanjappa ASHWATH. Biofuels Production through Biomass Pyrolysis —A Technological Review. *Energies*. 2012, 5(12), 4952-5001. DOI: 10.3390/en5124952. ISSN 1996-1073. Available at: <http://www.mdpi.com/1996-1073/5/12/4952>
44. WEERACHANCHAI, Piyarat, Chaiyot TANGSATHITKULCHAI a Malee TANGSATHITKULCHAI. Fuel Properties and Chemical Compositions of Bio-Oils from Biomass Pyrolysis. *SAE Technical Papers*. 2007, 2007-07-23, , -. DOI: 10.4271/2007-01-2024. Available at: <https://www.sae.org/content/2007-01-2024/>
45. BRIDGWATER, Tony. Challenges and Opportunities in Fast Pyrolysis of Biomass: Part I. *Johnson Matthey Technology Review*. 2018, 62(1), 118-130. DOI: 10.1595/205651318X696693. ISSN 2056-5135. Available at: <http://www.ingentaconnect.com/content/10.1595/205651318X696693>
46. BFB Reactor Technology [Figure] MARSHALL, A. J. Commercial Application of Pyrolysis Technology in Agriculture. Ontario, Canada, 2013. Available at: <https://ofa.on.ca/wp-content/uploads/2017/11/Pyrolysis-Report-Final.pdf>
47. MARSHALL, A. J. Commercial Application of Pyrolysis Technology in Agriculture. Ontario, Canada, 2013. Available at: <https://ofa.on.ca/wp-content/uploads/2017/11/Pyrolysis-Report-Final.pdf>
48. BRIDGWATER, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*. 2012, 38, 68-94. DOI: 10.1016/j.biombioe.2011.01.048. ISSN 09619534. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0961953411000638>
49. Circulating Fluidized Bed Reactor Technology [Figure] MARSHALL, A. J. Commercial Application of Pyrolysis Technology in Agriculture. Ontario, Canada, 2013. Available at: <https://ofa.on.ca/wp-content/uploads/2017/11/Pyrolysis-Report-Final.pdf>

50. VERMA, M., S. GODBOUT, S. K. BRAR, O. SOLOMATNIKOVA, S. P. LEMAY a J. P. LAROUCHE. Biofuels Production from Biomass by Thermochemical Conversion Technologies. *International Journal of Chemical Engineering*. 2012, 2012, 1-18. DOI: 10.1155/2012/542426. ISSN 1687-806X. Available at: <http://www.hindawi.com/journals/ijce/2012/542426/>
51. Auger/screw pyrolysis reactor concept using heat carrier [Figure] VERMA, M., S. GODBOUT, S. K. BRAR, O. SOLOMATNIKOVA, S. P. LEMAY a J. P. LAROUCHE. Biofuels Production from Biomass by Thermochemical Conversion Technologies. *International Journal of Chemical Engineering*. 2012, 2012, 1-18. DOI: 10.1155/2012/542426. ISSN 1687-806X. Available at: <http://www.hindawi.com/journals/ijce/2012/542426/>
52. Our technology. BTG-BTL [online]. Enschede: BTG Biomass Technology Group, c2019 [cit. 2019-05-20]. Available at: <https://www.btg-btl.com/en/technology>
53. The Rotating cone reactor [Figure] Rotating cone. KTH Royal Institute of Technology [online]. Stockholm, Sweden: KTH Royal Institute of Technology, 2019 [cit. 2019-06-12]. Available at: http://energy.kth.se/compedu/webcompedu/webhelp/S9_Renewable_Energy/B4_Bioenergy/C3_Liquid_Biofuels/ID29_files/Rotating_cone.htm
54. GEORGIA TECH RESEARCH CORPORATION. Oil production by entrained pyrolysis of biomass and processing of oil and char. 1990. USA. 4891459. Filed 1986-01-17. Date of patent 1990-01-02.
55. RADLEIN, D. a A. QUIGNARD. A Short Historical Review of Fast Pyrolysis of Biomass. 2013, 68(4), 765-783. DOI: 10.2516/ogst/2013162. ISSN 1294-4475. Available at: <http://ogst.ifpenergiesnouvelles.fr/10.2516/ogst/2013162>
56. The Georgia Tech entrained flow pyrolysis system [Figure] RADLEIN, D. a A. QUIGNARD. A Short Historical Review of Fast Pyrolysis of Biomass. 2013, 68(4), 765-783. DOI: 10.2516/ogst/2013162. ISSN 1294-4475. Available at: <http://ogst.ifpenergiesnouvelles.fr/10.2516/ogst/2013162>
57. PISKORZ, Jan, Desmond RADLEIN a Piotr MAJERSKI. An improved process for the thermal conversion of biomass to liquids. European Union. 94900674.6.
58. Flow diagram—University of Waterloo [Figure] BRIDGWATER, A. V. a G. GRASSI. Biomass pyrolysis liquids: upgrading and utilisation. New York, NY, USA: Sole distributor in the USA and Canada, Elsevier Science Pub., c1991. ISBN 18-516-6565-X.

59. ENSYN TECHNOLOGIES INC. Aparatus for a circulating bed transport fast pyrolysis reactor system. 1999. USA. 5961786. Filed 1998-06-15. Date of patent 1999-10-05
60. Schematic representation of a fast pyrolysis flow System [Figure] ENSYN TECHNOLOGIES INC. Aparatus for a circulating bed transport fast pyrolysis reactor system. 1999. USA. 5961786. Filed 1998-06-15. Date of patent 1999-10-05.
61. MUGGEN, Gerhard. Fast Pyrolysis Bio-Oil Technology and Production: Presentation pyrolysis technology. Enschede, 2019.
62. RTD Technologies fast pyrolysis [Figure] Fast pyrolysis. BTG-BTL [online]. Enschede: BTG Biomass Technology Group, c2019 [cit. 2019-05-18]. Available at: <http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis>
63. GANSEKOELE, Elwin. BTG-BTL's pyrolysis technology. Enschede, 2011. Available at: https://www.btg-btl.com/en/references/pyrolysis_technology_comparison.pdf
64. Feedstock testing. BTG-BTL [online]. Enschede: BTG Biomass Technology Group, c2019 [cit. 2019-05-24]. Available at: <https://www.btg-btl.com/en/company/services/feedstocktest>
65. SMITH, Amanda D. a Gabriel LEGORBURU. Psychrometric properties for moist air. University of Utah, USA, 2017. Available at: <https://github.com/SSESLab/psychrometrics>
66. SMITH, Amanda D. The University of Utah [online]. Salt Lake City, USA: The University of Utah, C2019 [cit. 2019-07-30]. Available at: https://faculty.utah.edu/u0907633-Amanda_D._Smith/research/index.html
67. CARLSSON, Kurt a Firma ECOEXPOERT. Gas cleaning in flue gas from combustion of biomass. Växjö, Sweden, 2008. Available at: <https://pdfs.semanticscholar.org/5e23/bcb6462c09e45c6e5812369a3eb9c56d8916.pdf>
68. i-x diagram [Figure] SKOČILAS, Jan. i-x diagram. CTU in Prague, Faculty of Mechanical Engineering, Dpt. of Process Engineering, 2019. Available at: https://moodle-vyuka.cvut.cz/pluginfile.php/63258/mod_resource/content/1/i-x%20-20%2B160.pdf
69. PARK, Hoon Chae, Hang Seok CHOI a Ji Eun LEE. Heat transfer of bio-oil in a direct contact heat exchanger during condensation. Korean Journal of Chemical

- Engineering. 2016, 33(4), 1159-1169. DOI: 10.1007/s11814-015-0256-y. ISSN 0256-1115. Available at: <http://link.springer.com/10.1007/s11814-015-0256-y>
70. ZHANG, Lei. Multicomponent drop vaporization modeling of petroleum and biofuel mixtures. Iowa State University, 2011. <https://doi.org/10.31274/etd-180810-655>. Graduate Theses and Dissertations. Iowa State University.
71. MILLER, R.S. a J. BELLAN. A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics. Combustion Science and Technology. 2010, 126(1-6), 97-137. DOI: 10.1080/00102209708935670. ISSN 0010-2202. Available at: <http://www.tandfonline.com/doi/abs/10.1080/00102209708935670>
72. KRÁTKÝ, Lukáš. Gasification and Pyrolysis. CTU in Prague, Faculty of Mechanical Engineering, Dpt. of Process Engineering, 2019. Available at: https://moodle-vyuka.cvut.cz/pluginfile.php/63987/mod_resource/content/7/BBW_T5_Gasification%20and%20Pyrolysis.pdf
73. Stoichiometric Combustion Ratios. ALL Power Labs [online]. Berkeley, USA: ALL Power Labs, 2019 [cit. 2019-07-12]. Available at: <http://wiki.gekgasifier.com/w/page/6123822/Stoichiometric%20Combustion%20Ratios>
74. KOVÁCS, V. B. a A. MEGGYES. Investigation of Utilization of Low Heating Value Gaseous Fuels in Gas Engine. 2009. Available at: <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.566.861&rep=rep1&type=pdf>
75. Engineering ToolBox, (2004). Air - Molecular Weight and Composition. [online] Available at: https://www.engineeringtoolbox.com/molecular-mass-air-d_679.html [2019-06-14].
76. Highly Accurate and Precise Analysis. Celnis Analytical [online]. Plassey, UK: Celnis Limited, c2019 [cit. 2019-06-27]. Available at: <https://www.celnis.com/precision.php>
77. RAGLAND, K.W., D.J. AERTS a A.J. BAKER. Properties of wood for combustion analysis. Bioresource Technology. 1991, 37(2), 161-168. DOI: 10.1016/0960-8524(91)90205-X. ISSN 09608524. Available at: <https://linkinghub.elsevier.com/retrieve/pii/096085249190205X>

78. JANSE, Arthur M. C., Harald G. DE JONGE, Wolter PRINS a Wim P. M. VAN SWAAIJ. Combustion Kinetics of Char Obtained by Flash Pyrolysis of Pine Wood. *Industrial & Engineering Chemistry Research*. 1998, 37(10), 3909-3918. DOI: 10.1021/ie970705i. ISSN 0888-5885. Available at: <https://pubs.acs.org/doi/10.1021/ie970705i>
79. Circular of the Bureau of Standards no. 564: tables of thermal properties of gases comprising tables of thermodynamic and transport properties of air, argon, carbon dioxide, carbon monoxide hydrogen, nitrogen, oxygen, and steam. U.S. Department of Commerce: U.S. Department of Commerce, 1955.
80. SIMPSON, William a Anton TENWOLDE. Physical properties and moisture relations of wood. *Wood handbook: Wood as an engineering material*. 1999, GTR-113, 3.1-3.24.
81. Engineering ToolBox, (2003). Specific Heat of common Substances. [online] Available at: https://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html [2019-05-24]
82. Engineering ToolBox, (2010). Water - Heat of Vaporization. [online] Available at: https://www.engineeringtoolbox.com/water-properties-d_1573.html [2019-07-02].
83. VAN DE VELDEN, Manon, Jan BAEYENS, Anke BREMS, Bart JANSSENS a Raf DEWIL. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy*. 2010, 35(1), 232-242. DOI: 10.1016/j.renene.2009.04.019. ISSN 09601481. Available at: <https://linkinghub.elsevier.com/retrieve/pii/S0960148109001803>
84. VAN DE BELD, L. a G. MUGGEN. Empyro: Implementation of a commercial scale fast pyrolysis plant in the Netherlands. 23rd European Biomass Conference and Exhibition. 2015, , 1670-1673.
85. SVOBODOVÁ, Kateřina, Head of the Laboratory of Petrochemistry in Unipetrol výzkumně vzdělávací centrum, a.s. - UniCRE [Correspondence and analysis report]. Litvínov, 2019-07-26.
86. CZERNIK, S. a A. V. BRIDGWATER. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy&Fuels*. 2004, 18(2), 590-598. DOI: 10.1021/ef034067u. ISSN 0887-0624. Available at: <https://pubs.acs.org/doi/10.1021/ef034067u>
87. Bromové číslo. *Petroleum.cz* [online]. Prague: UCT in Prague, Dpt. of Petroleum Technology and Alternative Fuels, 2019 [cit. 2019-07-29]. Available at: <http://www.petroleum.cz/slovník.aspx?pid=66>

88. OYEBANJI, J.A., P.O. OKEKUNLE, O.A. LASODE a S.O. OYEDEPO. Chemical composition of bio-oils produced by fast pyrolysis of two energy biomass. *Biofuels*. 2017, 9(4), 479-487. DOI: 10.1080/17597269.2017.1284473. ISSN 1759-7269. Available at:
<https://www.tandfonline.com/doi/full/10.1080/17597269.2017.1284473>
89. SHENG, Changdong a J.L.T. AZEVEDO. Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass and Bioenergy*. 2005, 28(5), 499-507. DOI: 10.1016/j.biombioe.2004.11.008. ISSN 09619534. Available at:
<https://linkinghub.elsevier.com/retrieve/pii/S0961953404002107>
90. PAPARI, Sadegh a Kelly HAWBOLDT. A review on condensing system for biomass pyrolysis process. *Fuel Processing Technology*. 2018, 180, 1-13. DOI: 10.1016/j.fuproc.2018.08.001. ISSN 03783820. Available at:
<https://linkinghub.elsevier.com/retrieve/pii/S0378382018310142>
91. ZHANG, Laibao, Zhenghong BAO, Shunxiang XIA, Qiang LU a Keisha WALTERS. Catalytic Pyrolysis of Biomass and Polymer Wastes. *Catalysts*. 2018, 8(12), 1-45. DOI: 10.3390/catal8120659. ISSN 2073-4344. Available at:
<http://www.mdpi.com/2073-4344/8/12/659>
92. PINHO, Andrea de Rezende, Marlon B.B. DE ALMEIDA, Fabio Leal MENDES, Vitor Loureiro XIMENES a Luiz Carlos CASAVECHIA. Co-processing raw bio-oil and gasoil in an FCC Unit. *Fuel Processing Technology*. 2015, 131, 159-166. DOI: 10.1016/j.fuproc.2014.11.008. ISSN 03783820. Available at:
<https://linkinghub.elsevier.com/retrieve/pii/S0378382014004755>
93. PERRY, Robert H., Don W. GREEN a James O. MALONEY. *Perry's chemical engineers' handbook*. 7th ed. New York: McGraw-Hill, c1997. ISBN 00-704-9841-5.

LIST OF FIGURES

Figure 1: Waste treatment and disposal in the European Union	5
Figure 2: Competing model scheme.....	12
Figure 3: Secondary cracking model.....	12
Figure 4: Active cellulose model	13
Figure 5: Semi-global model.....	14
Figure 6: Reaction example.....	14
Figure 7: Bubbling fluid bed reactor scheme	18
Figure 8: Circulating Fluidized Bed Reactor scheme	19
Figure 9: Screw reactor	20
Figure 10: Rotating cone reactor design.....	21
Figure 11: Georgia Tech entertained bed process scheme	22
Figure 12: Waterloo flash pyrolysis process scheme	23
Figure 13: Ensyn process scheme	24
Figure 14: BTG process scheme	25
Figure 15: Proposed model block scheme.....	27
Figure 16: Drying section.....	28
Figure 17: Pyrolysis section	29
Figure 18: Oil section.....	30
Figure 19: Combustion section	31
Figure 20: Reaction process	33
Figure 21: Mollier chart for dryer T-101.....	36
Figure 22: Sankey diagram for energy balance.....	42
Figure 23: Simulated distillation curve	50

LIST OF TABLES

Table 1: Waste production worldwide	4
Table 2: Waste production in the European Union	4
Table 3: Waste production in the Czech Republic	4
Table 4: Example of pyrolysis gas composition	38
Table 5: Pyrolysis bio-oil composition	47
Table 6: Pyrolysis oil samples properties.....	48

LIST OF ANNEXES

Annex 1: Mass and energy balances

Annex 2: Critical moisture

Annex 3: Process flow diagram

Annex 1: Mass and energy balances

```
clear all
clc
```

PROPERTIES

```
cps = 0.83; % sand specific heat capacity kJ/kgK
cpg = 1.1; % gas specific heat capacity kJ/kgK
cpa = 1.06; %air specific heat capacity kJ/kgK
cpash=1;
rhog=1.1; % gas density UNUSED?
rhoa=1.1; %air density UNUSED?
hevap=2256.4; %kJ/Kg latent heat of water evap. 100 °C
hrec=400; %kJ/kg
Mg=30; %gas molar mass kg/kmol Model_14
Ma=29; %air molar mass
TR = 480; % reaction temperature
Tok = 20; %surrounding temperature
Toilc=60; %oil condensation temperature°C
```

INPUT

```
mbin = 1000; % input biomass flow kg/hod
wbin = 40; % biomass moisture % weight
```

DRYING

```
wbout = 5; % required output biomass moisture %
mwout = mbin*(wbin-wbout)/100; % water flow output kg/hod
mbdry = mbin-mwout; % biomass flow output kg/hod
```

REACTOR - comparative model (function reakce7.m)

```
M0=[mbdry 0 0 0];
time=0:0.001:3;
[t,x]=ode23s(@reakce7,time,M0);
x1m=100.*x./mbdry;
tR=2.5;
tRvis=tR.*(ones(101,1));
tRvis2=(0:1:100);
figure (1)
plot(time,x1m,'Linewidth',2)
hold on
plot(tRvis,tRvis2,'k','Linewidth',0.5);
```



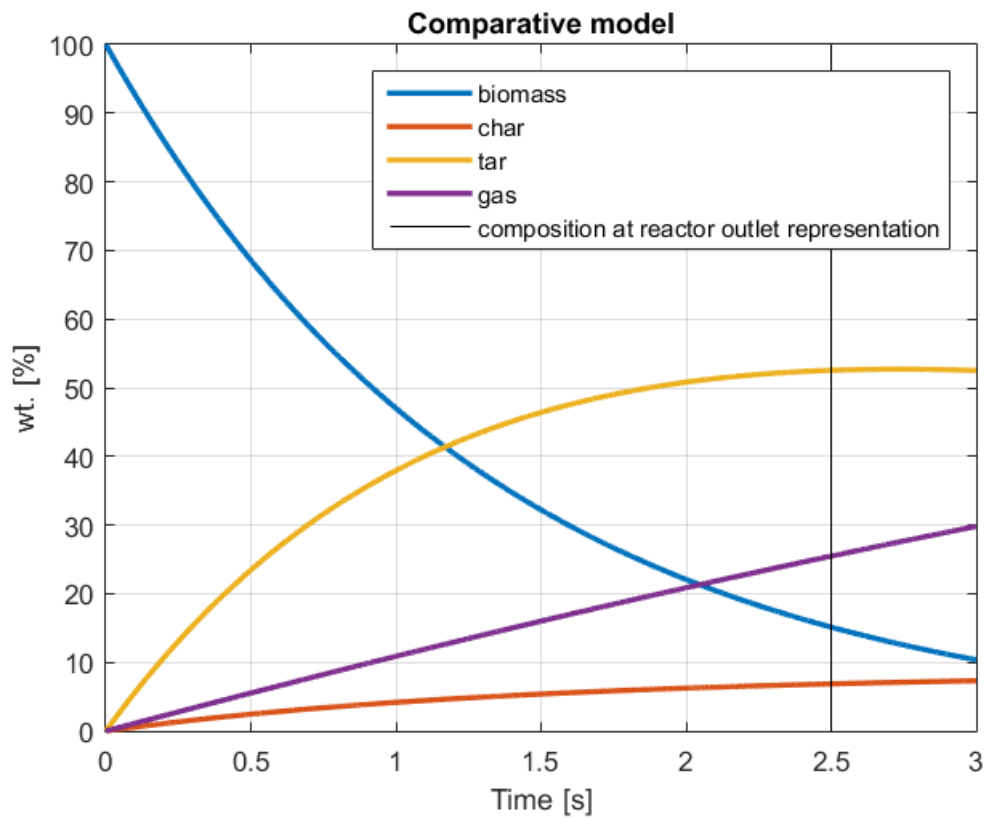
```

Legend('biomass','char','tar','gas','composition at reactor outlet representation')
grid on
title('Comparative model')
xlabel('Time [s]')
ylabel('wt. [%]')
hold off
tRindex=tR/(time(2)-time(1));

mbr=x(tRindex,1);
mcr=x(tRindex,2);
mlr=x(tRindex,3);
mgr=x(tRindex,4);

cpb=cpbmean((TR+Tok)/2);
Ereq=(mbdry/3600*cpb*(TR-Tok)+mbdry*wbout/100/3600*hevap+hreac*(mbdry*(1-wbout/100)-
mbr)/3600);

```



COMBUSTION reaction 1

```

LHVg=9.49*1000;
cch4=0.08;
cco2=0.2;
cco=0.2;
ch2=0.38;
cn2=0.14;

Mch4=16.04;
Mco2=44.01;

```

```

Mco=28.01;
Mh2=2.02;
Mn2=28;

Mg=cch4*Mch4+cco2*Mco2+cco*Mco+ch2*Mh2+cn2*Mn2;
mg=101.325*1*Mg/8.314/273;
LHVg=LHVg/mg;

LHVb=15.6*1000;

LHVC=27.5*1000;

ECR1=LHVC*mcr/3600; % Energy from char combustion kw
EgR1=LHVg*mgr/3600; %Energy from pyro gas combustion kw
EbR1=LHVb*mbr/3600; %Energy from biomass combustion kw

Egain=ECR1+EgR1+EbR1; %kw Energy from combustion
EbalanceR1 = ECR1+EgR1+EbR1-Ereq; % MW energy balance - positive good, negative bad
oilYieldR1 = mlr/(mlr+mcr+mgr)*100; %weight yield of oil

```

ENERGY COMBUSTION

```

Toc=850; %°C combustion temperature

Vg=mgr/Mg;
lambda=1.5;
no2=lambda*(cco*0.5+ch2*0.5+cch4*2)*Vg;
mair=no2/21*100*Ma+6*(mcr+mbr);

wbash=4; % %ash in biomass
wcash=7; %%ash v char

mash=mbr*wbash/100+mcr*wcash/100; % ash flow kg/hod
mflue=mair+mgr+mbr+mcr-mash; %fluegas flow kg/hod

Qa=mair/3600*(Toc-Tok)*cpa; % kw required to heat air
cpc=cpcmean((Toc+TR)/2);
Qc=mcr/3600*(Toc-TR)*cpc; % kw required to heat char
Qg=mgr/3600*(Toc-Toilc)*cpg; % kw required to heat gas
cpb=cpbmean((Toc+TR)/2);
Qb=mbr/3600*(Toc-TR)*cpb; % kw required to heat biomass

Qflue=mflue/3600*(Toc-Tok)*cpa; % kw to be taken out in flue gas

Eremaining=Egain-Qc-Qg-Qa-Qb-Qflue; % kw available power in combustion chamber
Efluegascooler=Qflue; %kw in flue gas output

```

SAND COOLER

```

ms=Eremaining/cps/(Toc-TR);
Qscool=Eremaining-Ereq;
Tscooler=Ereq/ms/cps+TR;

```

DRYER

```
TDB0 = 20; %°C
RH0=70; %%
p=101.325; %kpa
[h0,x0]=psych(TDB0,RH0,p);
TDB1=80;
RH1=0:0.001:100;

for i=1:length(RH1)
    [h1t(i),x1t(i),w1t(i),p1t(i)]=psych(TDB1,RH1(i),p);
end
j=1;
while abs(x0-x1t(j))>0.00001
    j=j+1;
end
h1=h1t(j);
x1=x1t(j);

TDB2=0:0.0001:TDB1;
RH2=70;

for k=1:length(TDB2)
    [h2t(k),x2t(k),w2t(k),p2t(k)]=psych(TDB2(k),RH2,p);
end
l=1;
while abs(h1-h2t(l))>0.001
    l=l+1;
end

h2=h2t(l);
x2=x2t(l);

mdryair=mwout/(x2-x0); %kg/h air to dryer
Qdryer=mdryair/3600*(h1-h0); %kw to heat air
Qdryer;
BalanceDryer=Qflue-Qdryer;
```

OIL COOLER

```
hcond=840; %
Toilc=60; %°C
Toilb=200; %°C
cpoil=2.5; %kj/kgK
moilc=(mgr+m1r)/3600;
Qoilcond=hcond*m1r/3600+moilc*cpg*(TR-Toilc); %kw
moilloop=Qoilcond/(cpoil*(Toilc-Tok));
Qoildoch1=(m1r/3600+moilloop)*cpoil*(Toilc-Tok);
```

```

function dmdt = reakce7 (t,m)

A=[3.27e6 1.08e10 4.38e9 1e5 4.28e6];
E=[111.7 148 152.7 108 108].*1000;
T=480+273;

R=8.314;

k=A.*exp(-E./(R*T));

dmdt=zeros(4,1);

dmdt(1)=m(1)*(-k(1)-k(2)-k(3)); %biomass
dmdt(2)=m(1)*k(1)+m(3)*k(4); %char
dmdt(3)=m(1)*k(2)-m(3)*k(4)-m(3)*k(5); %liquid
dmdt(4)=m(1)*k(3)+m(3)*k(5); %gas

end

```

Published with MATLAB® R2015a

```

function cpb = cpbmean(T)
% Simpson and Tenwolde (1999)
T=T+273.15;
cpb=0.1031+0.003867*T;
end

```

Published with MATLAB® R2015a

```

function cpc = cpcmean(T)
% Simpson and Tenwolde (1999)
T=T+273.15;
cpc=1.43+0.355e-3*(T)-7.32e4/(T)^2;
end

```

Published with MATLAB® R2015a

```

% Psychrometric properties for moist air
% https://github.com/SSESLab/psychrometrics
% provided dry bulb temperature (Celsius), relative humidity (%),
% and total atmospheric pressure (kPa)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Equations coded by Gabriel Legorburu%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Amanda D. Smith %
% amandasmith@gmail %
% Created 2017-07-19 %

```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
function [enthalpy, omega, wetbulb, Psat] = psych(DB_air_in,RH,p_kPa)
```

```
p_total = p_kPa*1000; % Convert to Pa
```

```
%%{Calculating air properties}%
```

```
%%{Coefficient values from ASHRAE fundamentals handbook section 1.12}%
```

```
c1=-5.6745359e+03;
```

```
c2=6.3925247e+00;
```

```
c3=-9.6778430e-03;
```

```
c4=6.2215701e-07;
```

```
c5=2.0747825e-09;
```

```
c6=-9.4840240e-13;
```

```
c7=4.1635019e00;
```

```
c8=-5.8002206e+03;
```

```
c9=1.3914993e+00;
```

```
c10=-4.8640239e-02;
```

```
c11=4.1764768e-05;
```

```
c12=-1.4452093e-08;
```

```
c13=6.5459673e00;
```

```
T=DB_air_in+273.15;
```

```
if DB_air_in >= 0
```

```
    pws=exp(c8/T+c9+c10*T+c11*T^2+c12*T^3+c13*log(T)); %Pa saturation pressure, EQN 6}%
```

```
    pw=0.01*RH*pws; %partial pressure of water vapor Eqn 24}%
```

```
    w_in=0.621945*pw/(p_total-pw); %humidity ratio Eqn 22}%
```

```
    ws=0.621945*pws/(p_total-pws); %moist air saturation ratio Eqn 23}%
```

```
    h_air_inlet=1.006*DB_air_in+w_in*(2501+1.86*DB_air_in); %kJ/kg, Eqn 32}%
```

```
if DB_air_in < 0
```

```
    pws=exp(c1/T+c2+c3*T+c4*T^2+c5*T^3+c6*T^4+c7*log(T)); %Pa saturation pressure, EQN 5}%
```

```
    pw=0.01*RH*pws; %partial pressure of water vapor Eqn 24}%
```

```
    w_in=0.621945*pw/(p_total-pw); %humidity ratio Eqn 22}%
```

```
    ws=0.621945*pws/(p_total-pws); %moist air saturation ratio Eqn 23}%
```

```
    h_air_inlet=1.006*DB_air_in+w_in*(2501+1.86*DB_air_in); %kJ/kg, Eqn 32}%
```

```
end
```

```
%Wet Bulb emperical equation from RH and DB: Wet-Bulb Temperature from
```

```
%Relative Humidity and Air Temperature, Roland Stull https://doi.org/10.1175/JAMC-D-11-0143.1
```

```
WB_air_in=DB_air_in*atan(0.151977*(RH+8.313659)^0.5)+atan(DB_air_in+RH)-atan(RH-1.676331)+0.00391838*RH^(3/2)*atan(0.023101*RH)-4.686035;
```

```
enthalpy = h_air_inlet; % Convert to kg
```

```
omega = w_in;
```

```
wetbulb = WB_air_in;
```

```
Psat = pws;
```

```
end
```

Annex 2: Critical moisture

```
clear all
clc
```

PROPERTIES

```
cps = 0.83;
cpg = 1.1;
cpa = 1.06;
cpash=1;
rhog=1.1;
rhoa=1.1;
hevap=2256.4;
hreac=400;
Mg=30;
Ma=29;
TR = 480;
Tok = 20;
Toilc=60;
```

INPUT

```
mbin = 1000; % input biomass flow kg/hod
wbinsug = 40:1:60; % biomass moisture % weight
for n=1:length(wbinsug)
```

```
    wbin=wbinsug(n);
```

DRYING

```
wbout = 5; % required output biomass moisture %
mwout = mbin*(wbin-wbout)/100; % water flow output kg/hod
mbdry = mbin-mwout; % biomass flow output kg/hod
```

REACTOR - comparative model (function reakce7.m)

```
M0=[mbdry 0 0 0];
time=0:0.001:3;
[t,x]=ode23s(@reakce7,time,M0);
x1m=100.*x./mbdry;
figure (1)
plot(time,x1m)
hold on
legend('biomass','char','tar','gas')
```

```

grid on
title('Comparative model')
close
tR=2.5;
tRindex=tR/(time(2)-time(1));

mbr=x(tRindex,1);
mcr=x(tRindex,2);
mlr=x(tRindex,3);
mgr=x(tRindex,4);

cpb=cpbmean((TR+Tok)/2);
Ereq=(mbdry/3600*cpb*(TR-Tok)+mbdry*wbout/100/3600*hevap+hreac*(mbdry*(1-wbout/100)-
mbr)/3600);

```

COMBUSTION reaction 1

```

LHVg=9.49*1000;
cch4=0.08;
cco2=0.2;
cco=0.2;
ch2=0.38;
cn2=0.14;

Mch4=16.04;
Mco2=44.01;
Mco=28.01;
Mh2=2.02;
Mn2=28;

Mg=cch4*Mch4+cco2*Mco2+cco*Mco+ch2*Mh2+cn2*Mn2;
mg=101.325*1*Mg/8.314/273;
LHVg=LHVg/mg;

LHVb=15.6*1000;

LHVc=27.5*1000;

Ecr1=LHVc*mcr/3600; % Energy from char combustion kw
Egr1=LHVg*mgr/3600; %Energy from pyro gas combustion kw
Ebr1=LHVb*mbr/3600; %Energy from biomass combustion kw

Egain=Ecr1+Egr1+Ebr1; %kw Energy from combustion
Ebalancer1 = Ecr1+Egr1+Ebr1-Ereq; % MW energy balance - positive good, negative bad
oilYieldR1 = mlr/(mlr+mcr+mgr)*100; %weight yield of oil

```

ENERGY COMBUSTION

```

Toc=850; %°C

Vg=mgr/Mg;
lambda=1.5;
no2=lambda*(cco*0.5+ch2*0.5+cch4*2)*Vg;

```

```

mair=no2/21*100*Ma+6*(mcr+mbr);

wbash=4;
wcash=7;

mash=mbr*wbash/100+mcr*wcash/100;
mflue=mair+mgr+mbr+mcr-mash;

Qa=mair/3600*(Toc-Tok)*cpa; % kw required to heat air
cpc=cpcmean((Toc+TR)/2);
Qc=mcr/3600*(Toc-TR)*cpc; % kw required to heat char
Qg=mgr/3600*(Toc-Toilc)*cpg; % kw required to heat gas
cpb=cpbmean((Toc+TR)/2);
Qb=mbr/3600*(Toc-TR)*cpb; % kw required to heat biomass

Qash=mash/3600*(Toc-Tok)*cpash; %kw to be taken out in ash
Qflue=mflue/3600*(Toc-Tok)*cpa; % kw to be taken out in flue gas

Eremaining=Egain-Qc-Qg-Qa-Qb-Qflue-Qash; % kw available power in flue gas
Efluegascooler=Qash+Qflue; %kw in flue gas output

```

SAND COOLER

```

ms=Eremaining/cps/(Toc-TR);
Qscon=Eremaining-Ereq;
Tsc cooler=Ereq/ms/cps+TR;

```

DRYER

```

TDB0 = 20; %°C
RH0=70; %%
p=101.325; %kpa
[h0,x0]=psych(TDB0,RH0,p);

TDB1sug=50:1:80;
for m=1:length(TDB1sug)
    TDB1=TDB1sug(m);
    RH1=0:0.1:100;

    for i=1:length(RH1)
        [h1t(i),x1t(i),w1t(i),p1t(i)]=psych(TDB1,RH1(i),p);
    end
    j=1;
    while abs(x0-x1t(j))>0.001
        j=j+1;
    end
    h1=h1t(j);
    x1=x1t(j);

    TDB2=0:0.1:TDB1;
    RH2=70;

    for k=1:length(TDB2)

```



```

[h2t(k),x2t(k),w2t(k),p2t(k)]=psych(TDB2(k),RH2,p);
end
l=1;
while abs(h1-h2t(l))>1
    l=l+1;
end

h2=h2t(l);
x2=x2t(l);

mdryair=mwout/(x2-x0);
Qdryer=mdryair/3600*(h1-h0);

BalanceDryer(m)=Qflue-Qdryer;
end
result(n)=max(BalanceDryer);
end
o=1;
while result(o)>0
    o=o+1;
end
wbincritical=wbinsug(o);

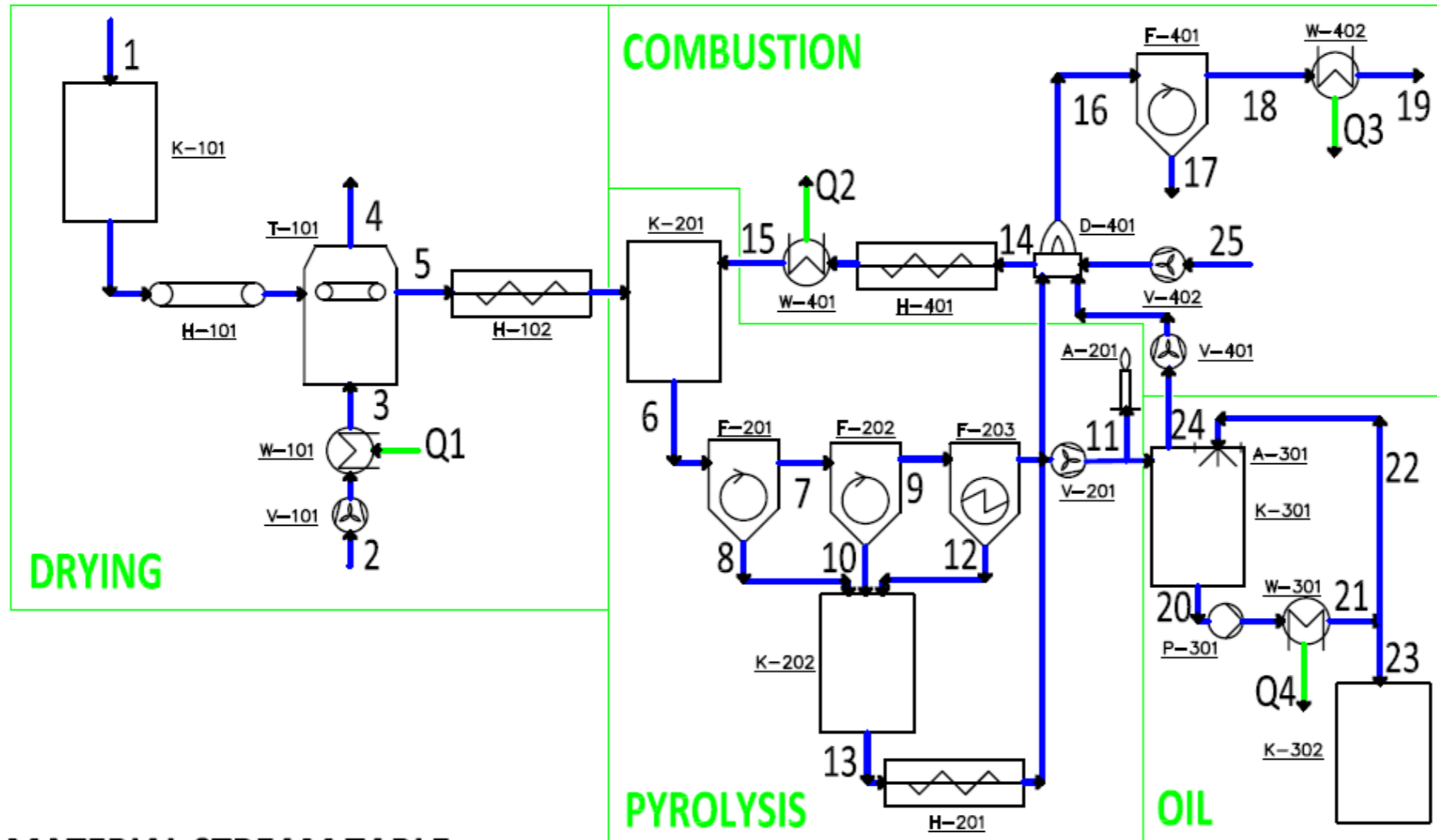
```

wbincritical =

47

[Published with MATLAB® R2015a](#)

Annex 3: Process flow diagram



EQUIPMENT TABLE

TAG	TYPE	DESCRIPTION
A-201	A	GAS FLARE
A-301	A	FLUID DISTRIBUTION DEVICE
D-401	D	BURNER FIRING SYSTEM
F-201	F	GENERAL SEPARATOR
F-202	F	CYCLONE SEPARATOR
F-203	F	ELECTROSTATIC PRECIPITATOR SEPARATOR
F-401	F	CYCLONE SEPARATOR
H-101	H	BELT CONVEYOR
H-102	H	SCREW CONVEYOR
H-201	H	SCREW CONVEYOR
H-401	H	SCREW CONVEYOR
K-101	K	GENERAL VESSEL
K-201	K	GENERAL VESSEL
K-202	K	GENERAL VESSEL
K-301	K	GENERAL VESSEL
K-302	K	GENERAL VESSEL
P-301	P	GENERAL PUMP
T-101	T	GENERAL DRIER
V-101	V	GENERAL BLOWER
V-201	V	GENERAL BLOWER
V-401	V	GENERAL BLOWER
V-402	V	GENERAL BLOWER
W-101	W	GENERAL HEAT EXCHANGER 1
W-301	W	GENERAL HEAT EXCHANGER 1
W-401	W	GENERAL HEAT EXCHANGER 1
W-402	W	GENERAL HEAT EXCHANGER 1

MATERIAL STREAM TABLE

STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
Design temperature [°C]	20	20	80	37	20	480	480	480	480	480	480	480	480	850	797	850	850	850	20	60	20	20	20	60	20	
COMPONENTS [kg/h]																										
Wood chips	650	0	0	0	650	98	15	83	2	12	0	2	98	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	350	0	0	350	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pyrolysis gas	0	0	0	0	0	507	507	0	507	0	507	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pyrolysis oil	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5552	5552	5211	341	0	0
Pyrolysis char	0	0	0	0	0	45	7	38	1	6	0	1	45	0	0	0	0	0	0	0	0	0	0	0	0	0
Sand	0	0	0	0	0	3477	522	2955	78	443	0	78	3477	3477	3477	0	0	0	0	0	0	0	0	0	0	0
Air	0	20211	20211	20211	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1615
Flue gas	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1917	0	1917	1917	0	0	0	0	0	0	0
Ash	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7	7	0	0	0	0	0	0	0	0	0
SUM [kg/h]	1000	20211	20211	20561	650	4127	1050	3077	588	462	507	81	3620	3477	3477	1924	7	1917	1917	5552	5552	5211	341	166	1615	

ENERGY STREAM TABLE

ENERGY STREAM	Q1	Q2	Q3	Q4
Power [kW]	345	42	468	154

DATE	2023.07.01	DATE	2023.07.01
DESIGNER	PROJEKTANT	CHECKER	PROJEKTANT
APPROVED	PROJEKTANT	APPROVED	PROJEKTANT
FAKULTA STROJNÍ		PROCESS FLOW DIAGRAM	
PFD-01		PFD-01	