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Generation of climate neutral secondary raw materials from bio-waste in Peru, using a self-constructed bench scale pyrolysis reactor

erstellt für

LEHRSTUHL FÜR ABFALLVERWERTUNGSTECHNIK UND ABFALLWIRTSCHAFT

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EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre an Eides statt, dass ich diese Arbeit selbständig verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und mich auch sonst keiner unerlaubten Hilfsmittel bedient habe.

AFFIDAVIT

I declare in lieu of oath, that I wrote this Thesis and performed the associated research myself, using only literature cited in this volume.

ACKNOLEDGMENT

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Kurzfassung

Erzeugung von klimaneutralen Sekundärrohstoffen aus Bioabfall in Peru mit einem selbst konstruierten Pyrolysereaktor im Labormaßstab

Das Wirtschaftswachstum in den letzten Jahren und die stabile politische Lage sind für eine solide Entwicklung in Peru mitverantwortlich. Dieser Fortschritt schafft aber auch neue Herausforderungen und einen höheren Energiebedarf des Landes. Pyrolyse scheint dabei eine vielversprechende Technologie für die Zukunft zu sein, um klimaneutrale Brennstoffe und Rohstoffe (z.B.: Kaffesud) aus Biomasseabfällen im Bereich Land- und Forstwirtschaft in Peru zu produzieren. Um das große Potenzial von organischen Abfällen zu nutzen, wurde ein Pyrolysereaktor im Labormaßstab an der Pontificia Universidad Católica del Perú (PUCP) errichtet. Erste Experimente mit Biomasse-Rohstoffen wurden durchgeführt, um Bio-Öl zu produzieren. Die vorliegende Arbeit beschreibt die Konstruktion und den Aufbau der PUCP-Flash-Pyrolyse-Pilotanlage in Peru. Darüber hinaus sind die Ergebnisse der grundlegenden Experimente und eine kurzen Charakterisierung der Produkte (Pyrolysekoks, Öl und Gas) aus der Pyrolyse dargestellt. Des weiterem werden konkrete Vorschläge für eine Fortsetzung des Projektes mit einer modifizierten größeren Pyrolyse-Anlage vorgelegt.

Abstract

Generation of climate neutral secondary raw materials from bio-waste in Peru, using a self-constructed bench scale pyrolysis reactor

The economic growth in the last years combined with a higher political stability is responsible for a stable development in Peru. This progress also creates new challenges and a higher energy demand in the country. Pyrolysis seems to be a very promising way of technology for the future to produce climate neutral fuels and raw materials from biomass waste in Peru. To use the large potential of organic waste, a bench scale pyrolysis reactor was constructed at the Pontificia Universidad Católica del Perú (PUCP). First experiments with biomass feedstock were made to produce bio-oil. This research work describes the construction and composition of the flash pyrolysis pilot plant in Peru. Furthermore the results of the first experiments with biomass are presented with a brief characterization of the products (biochar, oil and gas) obtained from the pyrolysis process.

Resumen

Generación de materias primas secundarias neutrales en carbono a partir de residuos biológicos en Perú utilizando un reactor de pirólisis en escala de laboratorio de construcción propia

El crecimiento económico en combinación con una mayor estabilidad política es responsable del desarrollo estable en Perú en el último año. Este progreso también trae nuevos retos y una mayor demanda de energía en el país. La pirólisis parece una forma de tecnología muy prometedora en el futuro para producir materias primas energéticas neutras en carbono a partir de residuos en el Perú. Para utilizar este gran potencial de los residuos orgánicos, un reactor de pirólisis en escala piloto fue construido en la Pontificia Universidad Católica del Perú PUCP. Se realizaron los primeros experimentos para producir bio - aceite. Este trabajo de investigación describe la construcción y la composición de la primera planta piloto de pirólisis flash en el Perú. Además, los resultados de los primeros experimentos son presentados con una breve caracterización de los productos (carbón, petróleo y gas) obtenidos del proceso de pirólisis.

Resumen

Translation to Quechua

El crecimiento económico en combinación con una mayor estabilidad política es responsable del desarrollo estable en Perú en el último año.

Estado allin apaykachaywan kuska qullqiyuq kay wiñariptin kay qhipa wataqa Piruw llaqtaqa wiñarintaq.

Este progreso también trae nuevos retos y una mayor demanda de energía en el país.

Kay wiñarisqanqa musuq aypanakunatam apamuntaq, hinallataq kay hatun llaqtapiqa energíaqa achkam ña munakunñataq.

La pirólisis parece una forma de tecnología muy prometedora en el futuro para producir materias primas energéticas neutras en carbono a partir de residuos en el Perú.

Pirólisis nisqaqa qhipa pachapaqqa ancha suyarisqa tecnología hinam Piruwpi materias primas energéticas neutras nisqa puchumanta hamusqa carbono hurqunapaq.

Para utilizar este gran potencial de los residuos orgánicos, un reactor de pirólisis en escala piloto fue construido en la Pontificia Universidad Católica del Perú PUCP.

Kay kawsay kaymanta hamuq puchukunap hatun kaynin apaykachanapaqqa, escala pilotopi churasqa reactor de pirolisis nisqaqa Pontificia Universidad Católica del Perú PUCP nisqa hatun yachaywasipi rurarqanmi.

Se realizaron los primeros experimentos para producir bio - aceite.

Bio – aceite nisqa hurqunapaqqa ñawpaq ruraykunam apakurqantaq.

Este trabajo de investigación describe la construcción y la composición de la primera planta piloto de pirólisis flash en el Perú.

Kay llamk'ayqa ñawpaq Piruwpi planta piloto de pirólisis flash nisqap kayninta rurakuyta riqsirichintaq.

Además, los resultados de los primeros experimentos son presentados con una breve caracterización de los productos (carbón, petróleo y gas) obtenidos del proceso de pirólisis.

Hinallataq, ñawpaq experimentokunap rurunkunaqa sapa rurukunamanta qillqaspa riqsirichisqam, (carbónmantapis, petroleomantapin gasmantapis); kaykunari pirolisista ruraspa hurqusqam.

Contents

1 Introduction

During the last decade, after the oil crisis in the 70s, the search for alternative energy strategies was accelerated by reported decreasing fossil fuel reserves and climate change, and reinforced by the Kyoto Protocol. The current scientific consensus is, that if atmospheric concentrations of greenhouse gases increase in this century, as it did last century, global ecosystems will be significantly affected so that they will not be the same like humanity knows them at the moment. For that reason, it is very important to find ways that people all over the world have access to technologies and methods for generating energy in the most eco-friendly and climate neutral way. Climate change is a complex combination and interaction between climatic, environmental, economic, political, institutional, social and technological processes.

Peru is a developing country which has to deal with social, infrastructural and environmental problems. In the last years, progress could be observed in this country but until now a lot of people do not have access to the public water system or electricity. Also, reforms in the educational systems are necessary to decrease the number of illiteracy rate. Another important task is the fight against insecurity, corruption and drug production. Despite of these problems, Peru has become a very interesting emerging market due to a steady constant economic growth and political stability. These positive changes also bring new challenges for the country, especially in the areas of sustainable development, environmental protection, equality and social justice. A growing industry goes hand in hand with the rising need for energy and more environmental pollution. For that reason, Peru must find new ways for a more sustainable generation of green energy combined with social justice. The renewable energies potential of Peru includes a wide and interesting range of possibilities.

Bioenergy, and especially liquid biofuels, seems to be a very promising solution on the way to energy independence, for rural areas development and the reduction of the greenhouse gases emissions. But, possible negative consequences from biofuels production should not be forgotten. The effects on food prices, economic growth, energy security, deforestation and climate change depend on the feedstock as well as on the production process and its local circumstances and should be considered within the selection process of the most appropriate technology.

One of the most interesting options is the use of organic wastes and other biomass for the production of secondary raw materials and generation of energy direct. In general, two procedures could be used for power generation from this biogenic feedstock: 1) combustion, and 2) production of environmental-friendly fuels, such as methane, ethanol, biodiesel, etc.

The problem is, that until now there is a lack of available and well working technologies for this kind of processes in Peru and only a few research projects are known to promote and stimulate the development of this kind of adapted technologies.

1.1 Background

The production of liquid fuels from biomass is of special interest because the Peruvian government began to create legal frameworks to raise the use of renewable energy, which means that normal fuels have to be mixed compulsory with biofuels. The Peruvian law is demanding an additive of:

- 5 % biodiesel in diesel since 2011, and
- 7.8 % ethanol in gasoline since 2010.

Until now, these legal demands cannot be fulfilled with the national production of biofuels. A very promising possibility for the production of advanced generation biofuels is the production of bio-oil by pyrolysis processes. In Peru, there is a lot of agricultural and forestry wastes abundant which can be used as feedstock for this kind of adapted technology.

Pyrolysis means thermal decomposition of organic material occurring in the absence of oxygen. Also, it is always one of the first steps in combustion and gasification processes followed by total or partial oxidation of the intermediate products. The pyrolysis process converts organic materials in char, bio-oil and gas.

Lower process temperatures and longer vapour residence times favour charcoal production. High temperature and longer residence time increase the biomass conversion to gas, but moderate temperatures and short vapour residence time are optimum conditions for producing liquids (i.e. bio-oil). Fast pyrolysis processes for liquid fuel production is of particular interest, as liquids are transportable and easy to store because of the good energy - bulk density relationship compared to other feedstock. The use of pyrolysis (i.e. climate neutral fuels production technology) products leads to a closed carbon cycle but if pyrolysis coke (biochar), a pyrolysis product, is used like a fertilizer, the result would be a negative carbon cycle.

Research and development of this technology is offering a very interesting option for the future production of secondary raw materials and the generation of renewable energy in Peru.

1.2 Hypothesis and objectives

1.2.1 Hypothesis

In Peru there are abundant unused organic wastes available that could be used as feedstock for generation of energy, if the appropriate technology would be available. The challenge is to construct a bench scale pyrolysis reactor with indigenous parts only to produce bio-oil from the available biomass in Peru to open an alternative way for a cleaner energy generation in the country and stimulate research and development work in this area.

1.2.2 Objectives

The project has had two main objectives, which are:

- To design and construct a bench scale pyrolysis reactor at the Pontificia Universidad Católica del Perú (PUCP) with materials only available on the Peruvian market.
- To prove that the pyrolysis reactor is functioning well by performing pyrolysis experiments with an organic waste that can be found both at the university and throughout the country.

Besides the main objectives there are various other specific goals:

- Establishing an inventory of the current situation of renewable energy and biomass in Peru.
- Calculate and design the reactor according to laboratory scale operation demands.
- Finding an appropriate biomass feedstock for the first fundamental experiments with the pyrolysis reactor.
- Performing the experiments with different process parameters in order to achieve the highest possible yield of pyrolysis oil.
- Evaluation and characterization of the different pyrolysis products obtained.
- Elaboration of proposals for improvements of the system and for a possible scale up.
- Publication of the results at national and international conferences and in recognized journals.

2 Biomass as a source of energy

Energy sources may be divided into three categories: fossil fuels, renewable sources and nuclear sources. Fossil fuels include coal, oil (petroleum) and natural gas. Wind, sun or hydropower are the most familiar forms of renewable energy. But the oldest source of green energy is biomass (plant material, animal waste, etc.), used since humanity learned the secret of making fire. Until now, its use for cooking and heating remains vital to the daily energy needs of over 2 billion people in developing countries (Table 1). [1]

Table 1: Estimated population in selected countries/regions depending on solid biomass for cooking [1]

Region	No. of people which are depending on biomass [million]	Share in total of population [%]
Sub-Saharan Africa	575	76
North Africa	4	3
India	740	69
China	480	37
Indonesia	156	72
Rest of Asia	489	65
Brazil	23	13
Rest of Latin America	60	23
World	2,528	52

Organic matter stores energy from the sun through a process called photosynthesis (Figure 1). In this process, the sun gives plants the needed energy to convert water and carbon dioxide into oxygen and sugars (carbohydrates). The reason why biomass is a renewable energy source is because its supplies are not limited when it is used in a responsible and sustainable way; while humanity exists, it is expected that trees and crops will always grow and organic waste will also always exist. [2]

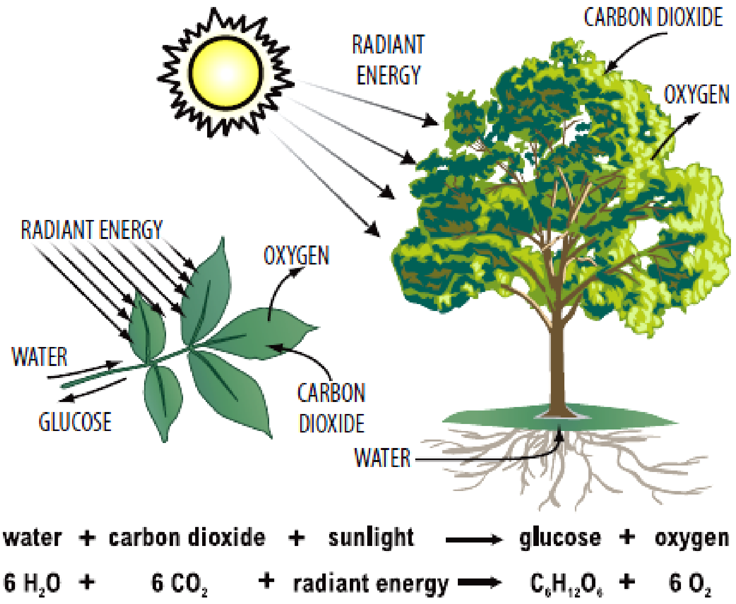


Figure 1: Simplified photosynthesis process [2]

2.1 Biomass sources

It is not easy to find a generally accepted definition on what is biomass. However, UNFCCC proposed the following definition relevant to this work [3]:

When referring to biomass in relevant baseline and monitoring methodologies:
(a) Biomass means non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material.
(b) Biomass residues mean biomass by-products, residues and waste streams from agriculture, forestry and related industries.

Biomass resources used for energy generation cover a wide range of materials and processes to convert organic material into energy. Actually, different energy needs are fulfilled with biomass including, for example, electricity generation, households heating and fuel for vehicles production as well as energy for industrial processes. Biomass is a result of plant growth in a direct or indirect way; that is why fossil fuels can also be termed as biomass since they are fossilized remains of plants. A classification for biomass sources is shown in Table 2. [4]

Table 2: Biomass sources classification [4]

Wastes	• agricultural production /processing wastes • crop residues • mill wood and organic wastes • urban organic wastes • animal and human biomass wastes (bones, meat-bone meal, chicken litter and others) • contaminated biomass and industrial biomass wastes (sewage sludge, hospital waste, paper-pulp sludge, municipal waste)
Forest products	• wood • logging residues • trees, shrubs and wood residues • sawdust, bark etc. from forest clearings
Energy crops	• short rotation woody crops • herbaceous woody crops • grasses • starch crops (corn, wheat and barley) • sugar crops (cane and beet) • forage crops (grasses, alfalfa and clover) • oilseed crops (oil palm, jatropha, safflower)
Aquatic plants	• algae • water weed and water hyacinth • reed and rushes

Energy generation from biomass can lead to a closed carbon cycle, because the plants are reducing CO_2 concentration in air by using the gas in photosynthesis. Therefore, biofuels contribute in the fight against global warming, but also other actions are necessary to face the challenge. [5] Figure 2 shows a positive carbon cycle, like today, and a closed carbon cycle like it should be in the future. [6]

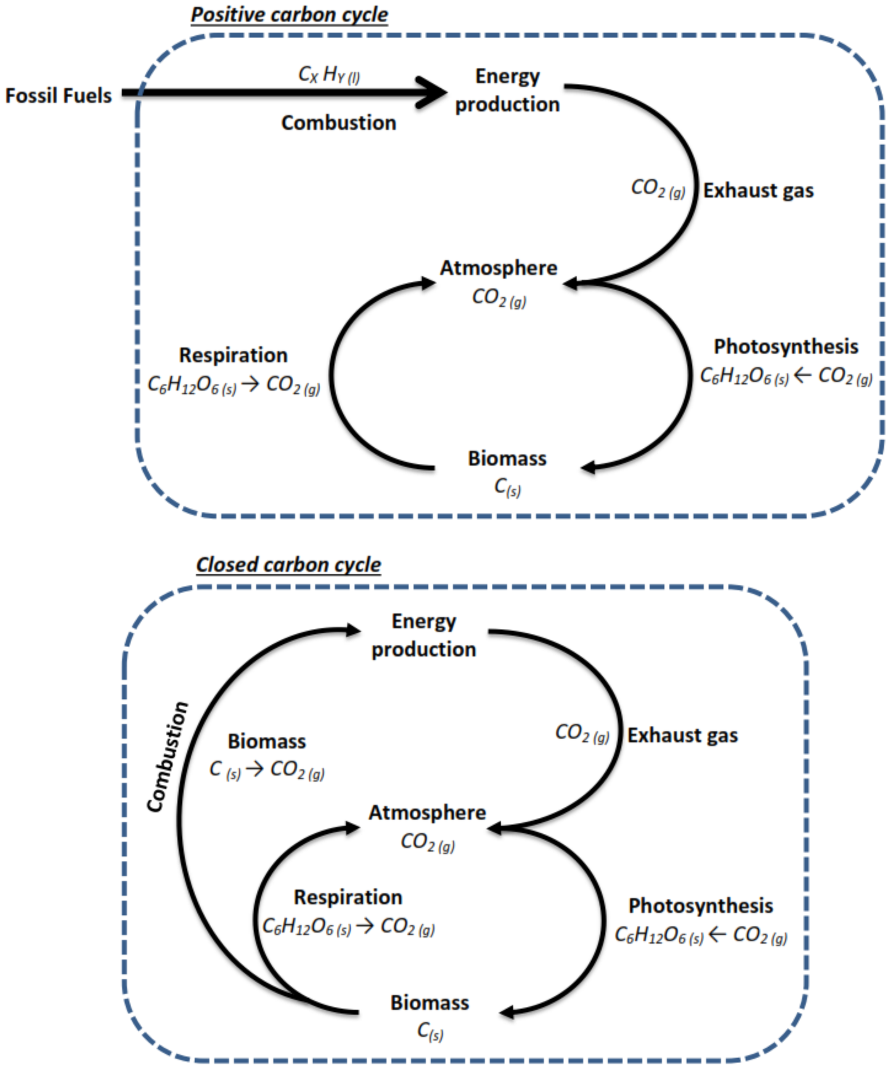


Figure 2: Positive and closed carbon cycle [6]

2.2 Biomass chemistry

The main primary components of biomass are cellulose, hemicellulose, lignin, starch, fats and proteins. Different kinds of biomass have distinctive components and physiochemical features vary in discrete fashion with their source; that is the reason why composition determines its use. Trees, for example, consist of cellulose, hemicellulose and lignin. On the other hand, grains contain starch, while livestock waste is composed by proteins and fats. There are also biomass types which are crops by-products, forest residues, construction and demolition wastes, municipal wastes, cattle and human wastes. [7] Cellulose, hemicellulose and lignin together form lignocellulose, a fibrous material that forms the cell walls of plants and trees, whereby bundles of fibers formed from cellulose give the strength. [8] Depending on biomass type, the composition of the biomass varies significantly why a lot of different molecules and structures exist. The examples of molecules presented in this chapter are the most common found in different references, but these are only examples of representatives of each group.

2.2.1 Cellulose

Cellulose is a polysaccharide composed of D-glucose, the most common organic compound on Earth and the primary structural part of cell walls in biomass. The general formula of this long polymer chain with high degree of polymerization and molecular weight is $(C_6H_{10}O_5)_n$ $(300 < n < 15.000)$. The crystalline structure (Figure 3) [7] consists of thousands of units made up of glucose molecules causing high strength. Humans cannot digest cellulose because its high insolubility in typical solvents like water, acids and ethanol.[9]

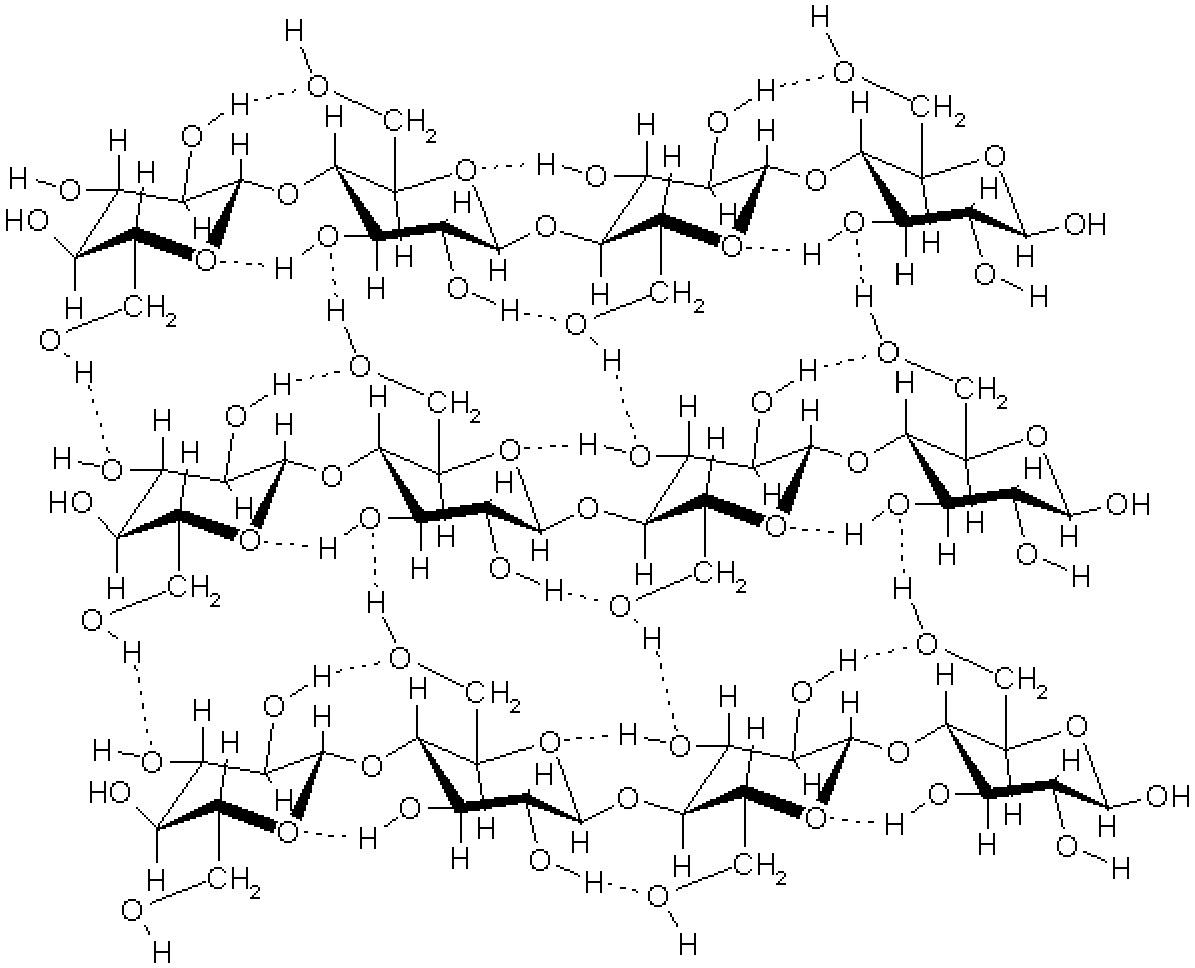


Figure 3: Chemical structure of cellulose [7]

2.2.2 Hemicellulose

Hemicellulose is a constituent of plant cell walls but has a random, amorphous structure. It is composed by carbohydrates with a branched chain structure and lower degree of polymerization than cellulose; its general formula is $(C_5H_8O_4)_n$ with $100 < n < 500$.

Depending on biomass type, the hemicellulose composition varies significantly. There are a lot of different molecular structures of hemicellulose because of a significant variation in the composition and structure among different biomass, a typical one is xylan which is shown in Figure 4. However, hemicellulose molecules also contain simple sugar residues like D-xylose, D-glycose or L-ababinose, among others. Many hemicelluloses are soluble in alkaline solutions.[9]

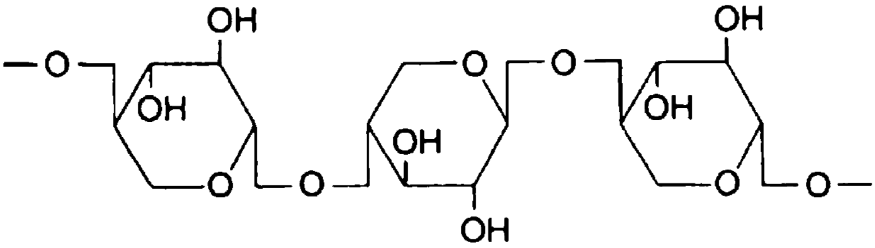


Figure 4: Molecular structure of a typical hemicellulose (xylan) [9]

2.2.3 Lignin

Lignin helps to bind the cellulose/hemicellulose matrix but also adds flexibility to the mix. The random disorganized polymer structure (Figure 5) consists mainly of aromatic carbon ring skeleton with methoxyl, hydroxyl and propyl groups. Lignin is one of the most abundant organic polymers and the third important constituent of the cell walls of wood. Even in sulfuric acid, lignin is highly insoluble. Cellulose, hemicellulose and lignin are the most abundant carbon resources and can be found in any kind of biomass. [9]

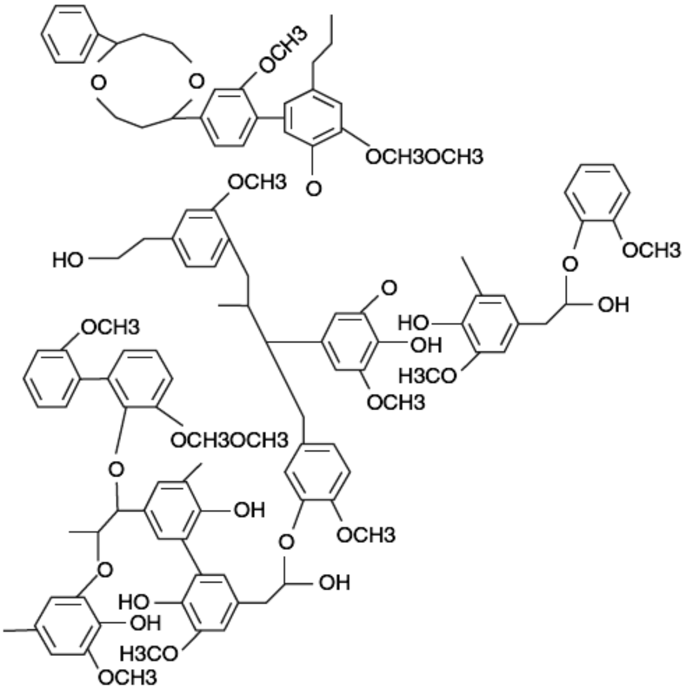


Figure 5: Possible lignin structure [9]

2.2.4 Starch

Starch is a polysaccaride with D-glucose units linked by α-glycosidic bonds, a very similar structure to cellulose (Figure 6). For that reason, solubility of some parts of starch molecule varies, per instance; amylose is soluble in hot water while amylopectin is insoluble in hot water. All green plants produce starch for energy storage. Starch has an important nutritional value and can be found in seeds, roots and stems. Starchy foods are a good source of energy and the main source of a range of nutrients in our diet. [7]

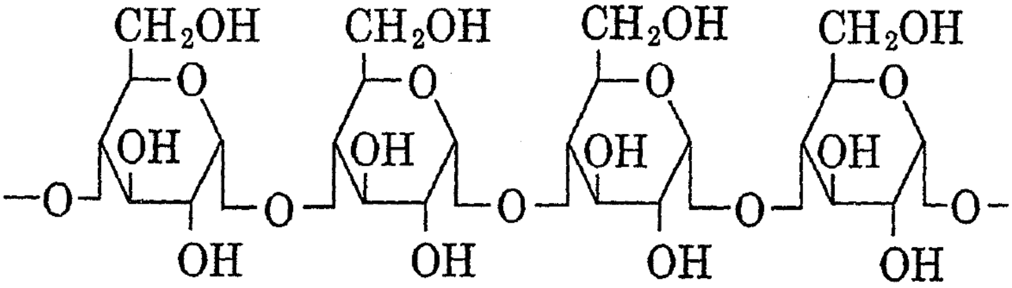


Figure 6: Starch sugar chain [7]

2.2.5 Other components

The amounts of other organic and inorganic components depend on specie and growth place. For example, proteins are macromolecular compounds with aminoacids highly polymerized. Other organic components are for example glycerides (i.e. fats) and sucrose. Representative examples for glycerides are vegetable oils (rapeseed oil, palm oil, etc.), and sugarcane or sugar beet for sucrose. Alkaloids, pigments, terpenes and waxes can be used pharmaceutically although they occur in very small amounts. [7]

2.3 Biofuels from biomass

In the last year, industry and scientists are looking for new ways to produce energy from different organic feedstock. The main conversion routes for biomass are shown in Figure 7. [10]

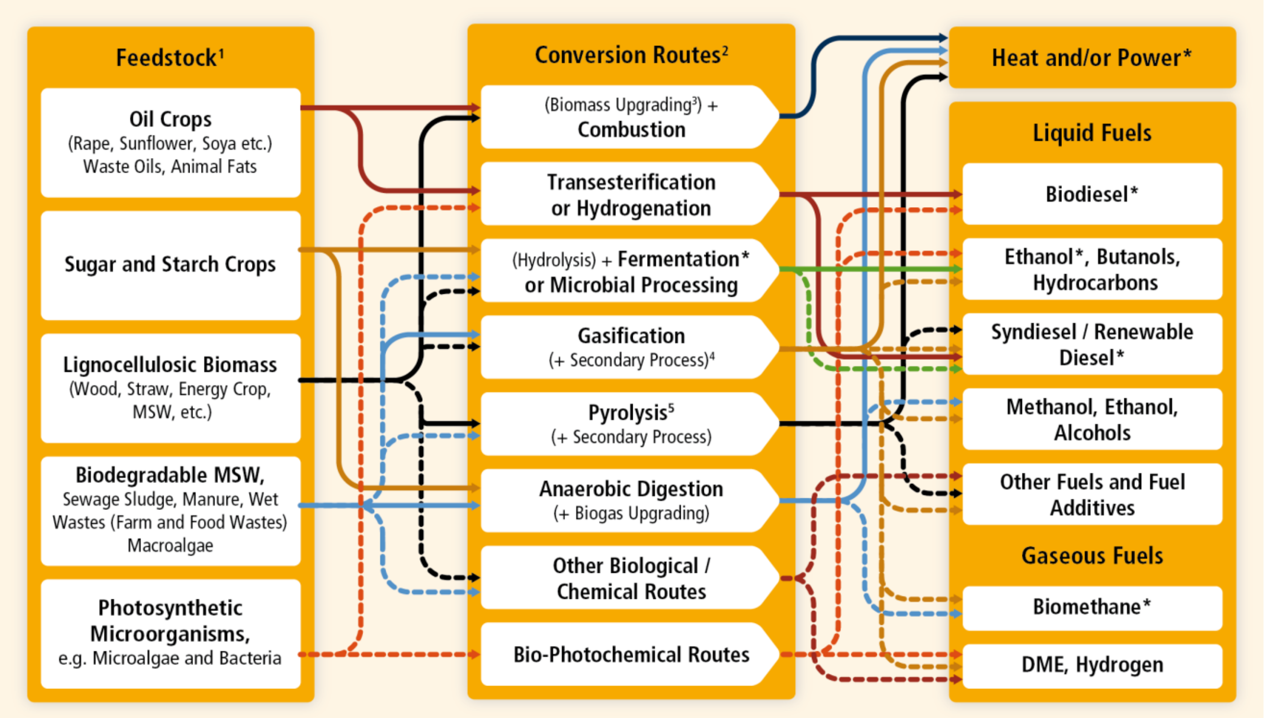


Figure 7: Schematic overview of the variety of commercial (solid lines) and developing bioenergy routes (dotted lines) from biomass feedstock through thermochemical, chemical, biochemical and biological conversion routes to heat, power, CHP (Combined Heat and Power) and liquid or gaseous fuels. [10]

Bioenergy and especially liquid biofuels have good reputations to enhance energy independence, help to develop rural areas and reduce greenhouse gases emissions. Without a balance of the positive and negative local impacts by biofuels it is not possible to draw conclusions. Specifically, effects on food prices, economic growth, energy security, deforestation and climate change depend on the feedstock as well as on the production process and its local circumstances. [11]

The interaction between bioenergy production and conventional production of other agricultural and forestry goods is shown in Figure 8 [10]. This correlation depends on natural conditions, agronomic and forestry practices and also on how people understand and prioritize nature conservation and protection of the ecological system. In developing countries the agricultural sector plays an important and critical role in supporting the livelihood and ensuring food security for the poorest. Concerted and coordinated strategies together with a good cooperation across different sectors are necessary for a sustainable development. Generally it could be said that the biofuel debate in developing countries has the tendency to focus on liquid biofuels and ignores other sources and possibilities for biofuels. Use of woody and residue biomass could benefit rural economies by providing employment as well as supplying energy to poor communities. [11]

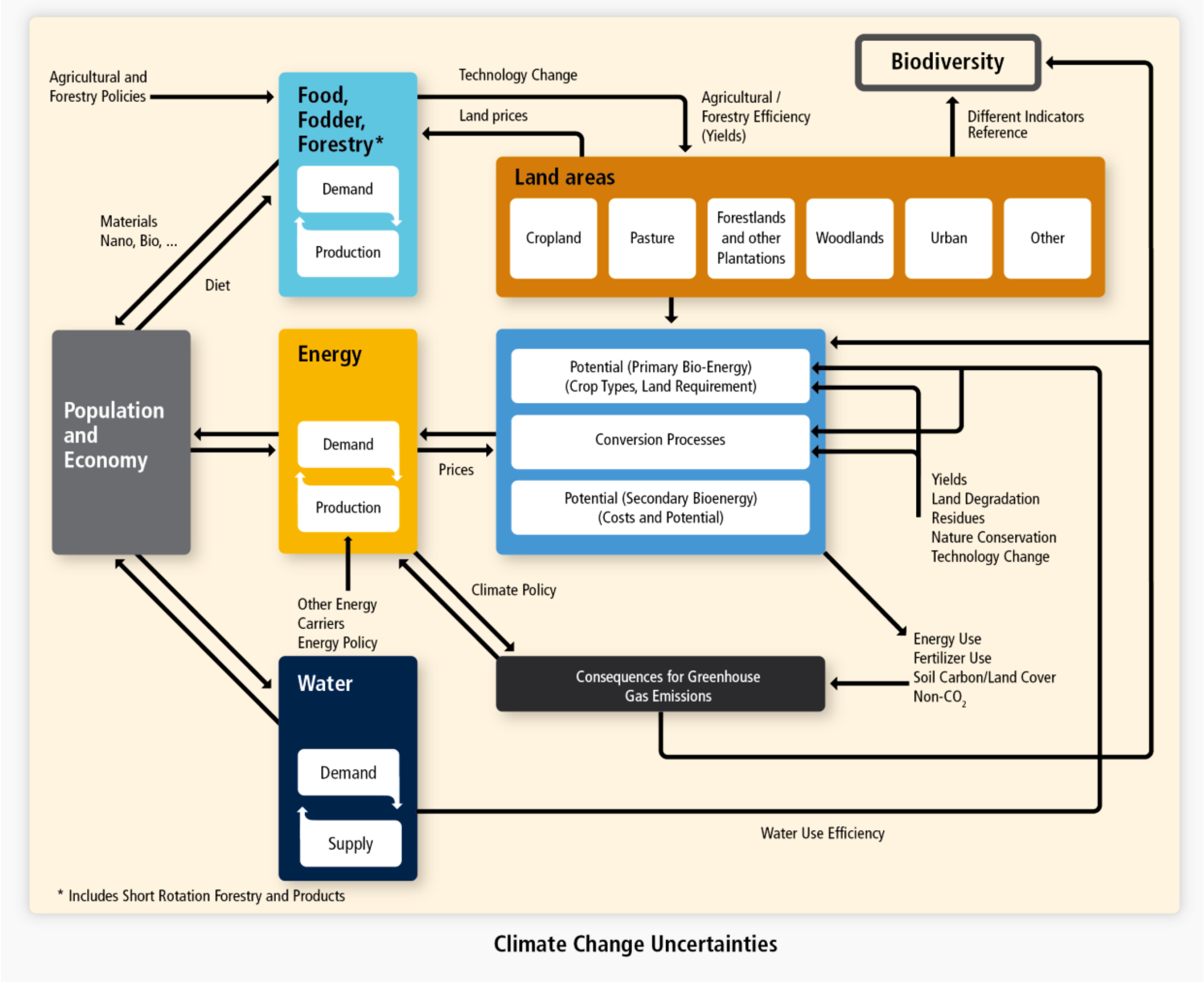


Figure 8: Overview of key relationships relevant to assessment of biomass resource potentials. Indirect land use and social issues are not displayed. [10]

Global bioethanol and biodiesel productions are presented in Figure 9 [12] and Figure 10 [13]. Figure 10 shows that global ethanol production is currently concentrated in two countries, Brazil and USA.

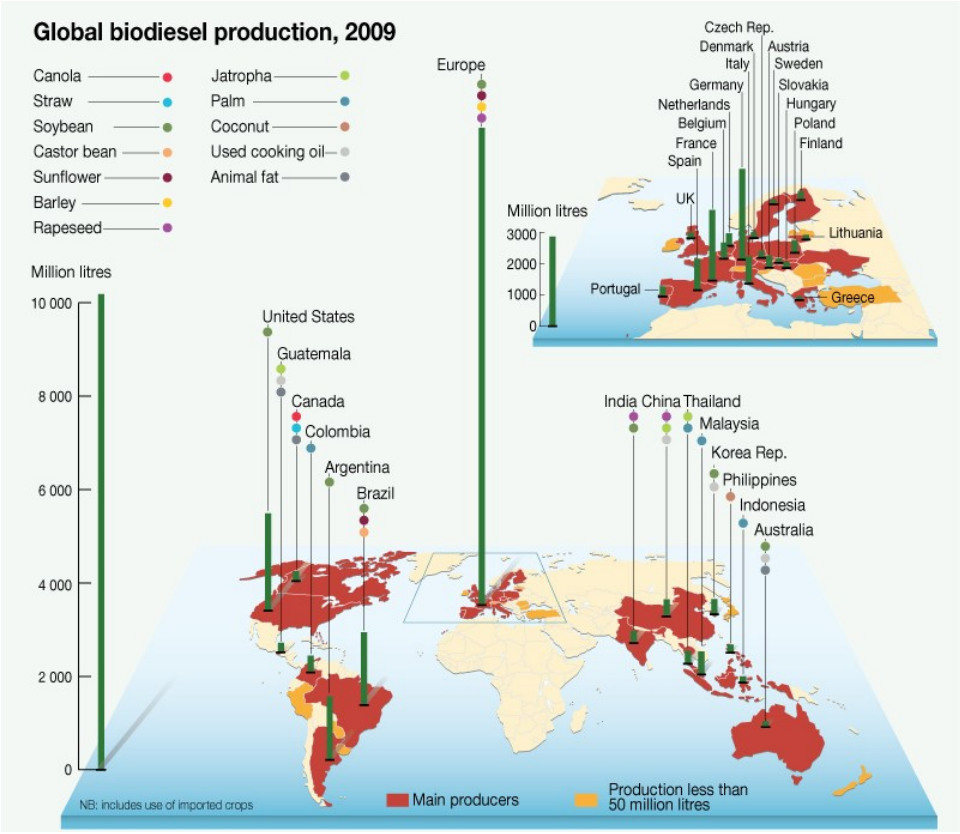


Figure 9: Global biodiesel production in the year 2009 [12]

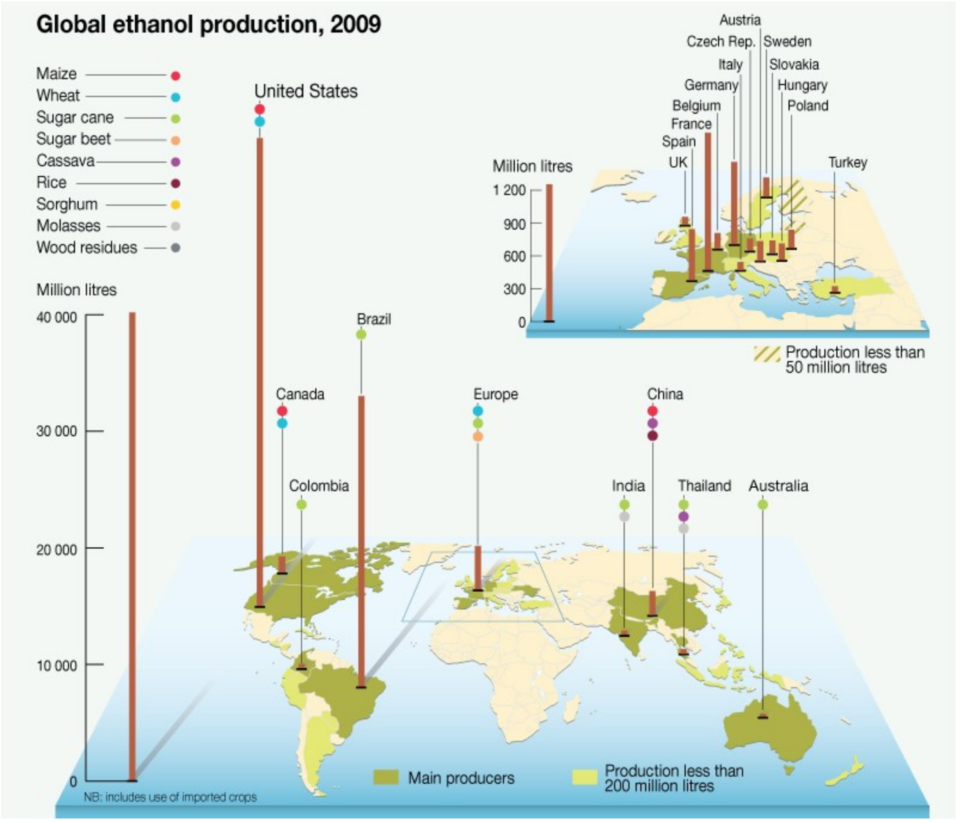


Figure 10: Global ethanol production, 2009 [13]

According to the current state of food and energy crisis, research and developments (R&D) in thermochemical processes, biodiesel and ethanol production technologies play an important role for a practical and sustainable energy solution. A sustainable farm-practice concept for waste management is a prerequisite to generate biofuels from farm residues fulfilling a variety of purposes: net greenhouse gas emissions reduction, solid waste reduction, carbon sequestration, soil enrichment and economic benefits, among others. [14]

2.3.1 First generation biofuels

First generation biofuels are made from sugar, starch or vegetable oil. They differ from "second generation biofuels" in their feedstock. The uses of these materials lead to discussion and negative impacts, some of them will be discussed in the next chapters. First generation biofuels are the "original" biofuels and constitute the majority of biofuels currently produced and used. The impacts of first generation biofuels are [15]:

a) Land use change

There are different forms of land use change, the direct and indirect loss of natural land. The direct land use change occurs when rainforest or other natural land is converted in cropland for biofuels production. The negative impacts are the loss of biodiversity and degradation of the soil. In a lot of cases this scenario also leads to a positive carbon cycle especially when the forests are burned to get farmland. The burning unleashes high amounts of CO_2 with a very negative impact on the carbon balance by life cycle analysis.[15] The potential risks of energy crop expansion on land access are shown in Figure 11 [16].

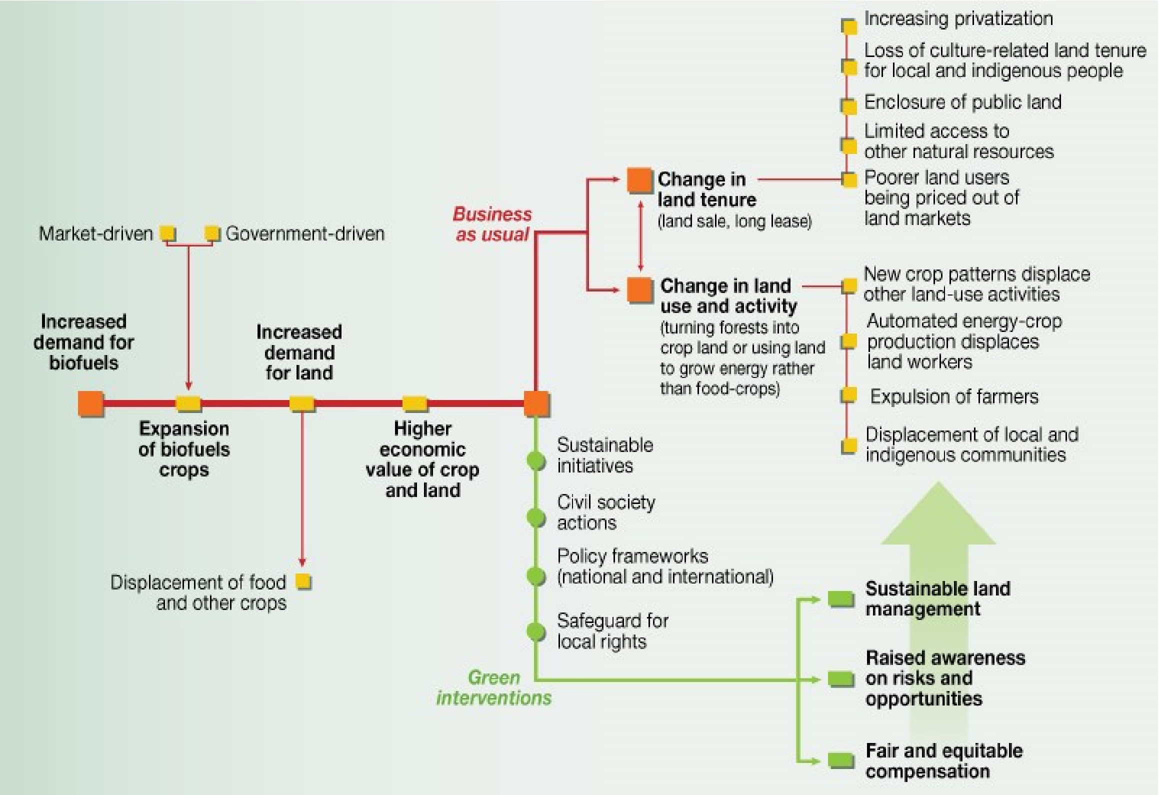


Figure 11: Potential risks of energy crop expansion on land access. [16]

The indirect land use change happens when the production of biofuels pushes other agricultural production into natural ecosystems. [15]

Life cycle analyses (LCA) of biofuel production in the Peruvian Amazon are showing that not all production ways make environmental sense. Different scenarios show that the fact that biofuel production is ecological or not depends strongly on the previous land use where energy crops are planted. The most harmful scenarios are those where primary forests are destroyed to get farmland for the energy crops. [17]

This can be shown with the carbon debt in 8 different scenarios calculated in the research of SNV. Positive environmental impact comes from oil palm and jatropha crops on degraded forest land with values of – 8.1 and - 9.5 tCO_2eq/ha, while biofuel production in primary forest incurs debts (the amount of years necessary using biodiesel, in order to compensate for the carbon emissions caused by the land use change to produce biodiesel) of 40 and 140 years for oil palm and jatropha, respectively. [17]

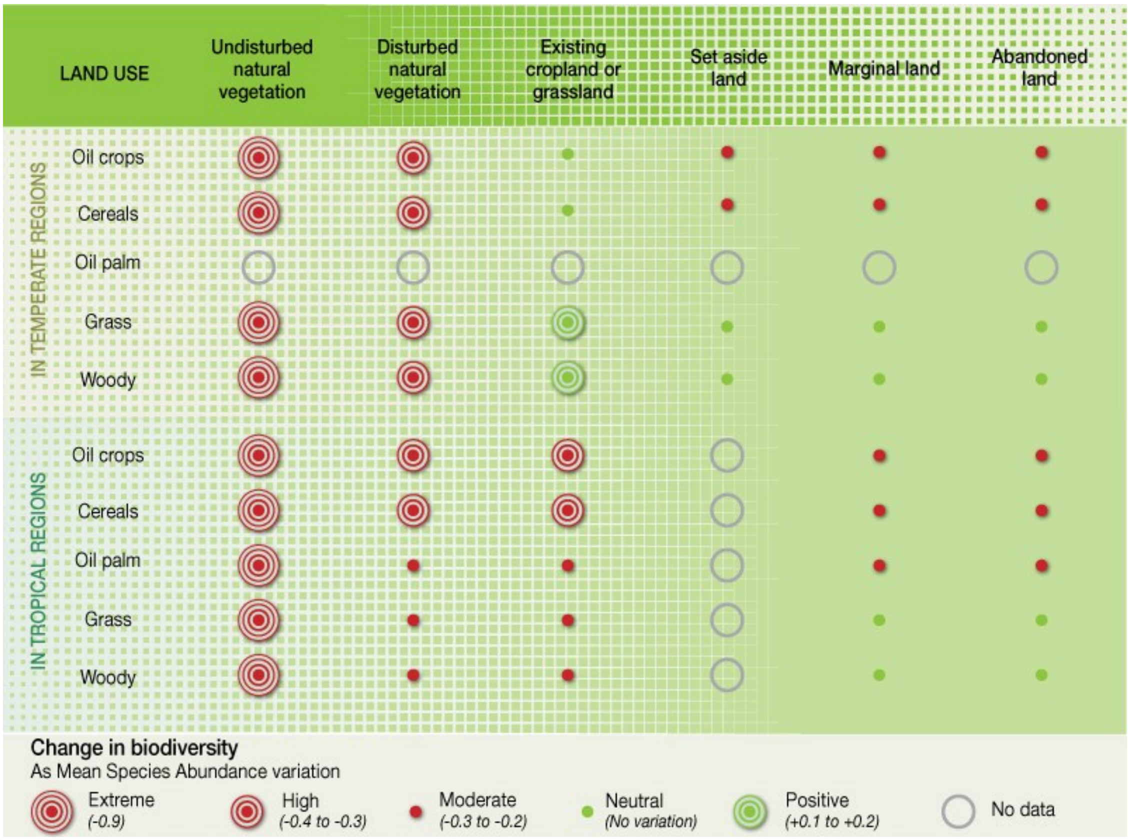
b) Food security

The most important and most discussed ethical issues in relation to biofuels are their impact on the food production. At the start of 2011 there were 925 million hungry people worldwide, whereby it always hits the poorest people the hardest life conditions. [18] Food crops are the most commonly used feedstock for first generation biofuels. The influence varies, they can be staple crops (*e.g.* corn, wheat), or key vegetable oils (*e.g.* palm oil). Also biofuel feedstock, like sugar cane, soybeans and rape seed are important inputs to the food industry. Consequently, it has been suggested that greater biofuel production can compete with food production both directly (*e.g.* food crops diverted for biofuel production) and indirectly (*e.g.* competition for land and agricultural labor). Not only the impact on the food offer is important, so are the effects on food prices. [15]

One example is the tortilla crisis in Mexico in 2007, when the prices of maize rose due to the increasing demand for maize for the production of ethanol in the USA because of the high oil prices. Tortillas cover over 50 % calories daily needed in Mexico, especially by poor people. With increasing prices, Mexicans could not afford their basic food and this led to social conflicts and protests.[19]

c) Monocultures / biodiversity

Monoculture means the growth of a single plant species over a large area of land, therefore natural living environment must be cleaned to make room for farmland eliminating a variety of species in the ecosystem. This also affects surrounding ecosystems by decreasing their health. The intensive processing required for monoculture leads to a high use of pesticides and fertilizers. A deterioration of soil quality and water balance is immediate consequence. In certain cases, it could be that the monoculture is stronger than their natural counterparts. So the monocropping can supplant those natural variants and further decrease biodiversity, mostly by genetically modified monocultures. The natural protection lack against wind makes monocultures weak against windstorms and erosion.[20] The short-term impact of land conversion on biodiversity is presented in Figure 12. Many factors are responsible for the impact degree, including location and production way. [21]



	LAND USE	Undisturbed natural vegetation	Disturbed natural vegetation	Existing cropland or grassland	Set aside land	Marginal land	Abandoned land
IN TEMPERATE REGIONS	Oil crops	◎	⊙	🟢	🔴	🔴	🔴
	Cereals	◎	⊙	🟢	🔴	🔴	🔴
	Oil palm	○	○	○	○	○	○
	Grass	◎	⊙	◉	🟢	🟢	🟢
	Woody	◎	⊙	◉	🟢	🟢	🟢
IN TROPICAL REGIONS	Oil crops	◎	⊙	⊙	○	🔴	🔴
	Cereals	◎	⊙	⊙	○	🔴	🔴
	Oil palm	◎	🔴	🔴	○	🔴	🔴
	Grass	◎	🔴	🔴	○	🟢	🟢
	Woody	◎	🔴	🔴	○	🟢	🟢

Change in biodiversity
As Mean Species Abundance variation
◎ Extreme *(-0.9)*
⊙ High *(-0.4 to -0.3)*
🔴 Moderate *(-0.3 to -0.2)*
🟢 Neutral *(No variation)*
◉ Positive *(+0.1 to +0.2)*
○ No data

Figure 12: Short-term impact of land conversion on biodiversity [21]

d) Water

Biofuels production requires high water amounts, first from energy plants production and later in the production process. For example, biofuels from corn have a water use per mile (with a car) from 283 gallons of water. [20] In countries like Peru, where for main production of agricultural products near the coast the water demand and water quality degradation are very important points. In general, the total water footprints are consistently large in developing countries. The water footprint for the production of conventional fossil fuels can be 70 – 400 times less than for biofuels. [22]

In summary, it can be said that for first generation biofuels production a lot of factors have to be considered. Biofuel production and use can affect different ecosystem services negatively or positively. The main ecosystem services affected are [22]:

- provisioning services (*e.g.* fuel, food, freshwater),
- regulating services (*e.g.* climate regulation, air quality regulation, erosion regulation),
- and cultural services.

A thorough and honest analysis of all social, environmental and economic factors and impacts are needed for each location to ensure a meaningful and sustainable production of biofuels (Figure 13). It is also clear that first generation fuels production is a chance for regional development processes. [23]

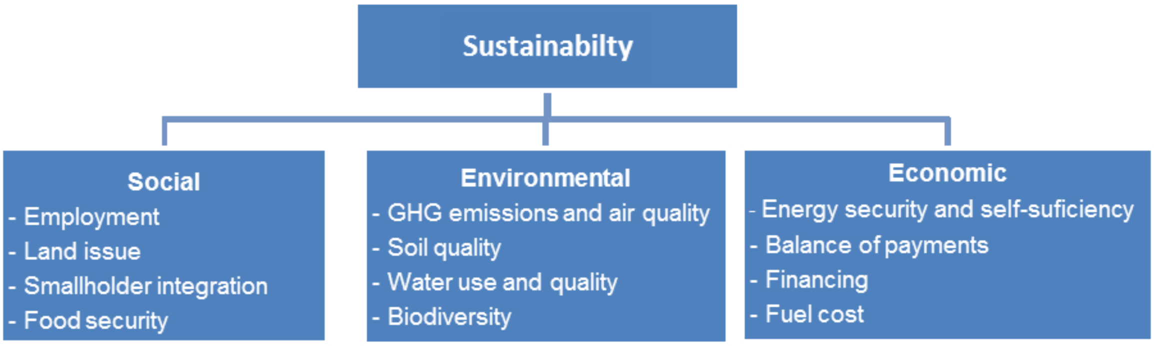


Figure 13: Different aspects for a sustainable biofuel and bioenergy production [23]

United Nations defined the following principles for a biofuel sustainability system to ensure compliance with sustainability principles and criteria [24]:

- negative GHG balance / carbon stock conservation
- biodiversity conservation / no destruction or damage to biodiversity / sustainable use of natural resources
- soil conservation / no soil degradation
- sustainable water use / no contamination or depletion of water
- air quality / no or reduced air pollution
- labor conditions / rights ensured according to international standards
- minimal impact on food prices / minimal competition with food production
- increased livelihoods of local populations
- minimal displacement / control and leakage.

2.3.2 Advanced biofuels

Advanced biofuels are biofuels that have the potential to be produced in large quantities and deliver a significant lifecycle GHG emission saving while minimizing competition for agricultural land. They also have potential to be economically competitive with conventional fossil fuels, for example today´s ethanol production from sugar cane in Brazil.

Typical feedstock for advanced biofuels are waste, agricultural (food crops) residues, non-food (ligno) cellulosic biomass, crops grown on marginal land, purpose-grown perennial grasses or trees and algae. [25] These technologies may offer the following advantages over the first generation biofuel processes:

- use of feedstock with lower land requirement and/or non-food raw materials;
- the conversion processes are more efficient;
- production of “fungible fuels” which can be mixed with conventional fuels;
- better overall greenhouse gas balances.

They also can be grouped into those produced either biochemically or thermochemically. Today, the best developed technologies for the production of advanced biofuels are at the point where the first commercial scale ups are starting to work, others are at the pre-commercial demonstration stage, and there are a lot still at earlier stages in the development life cycle. [26] Only a few large-scale facilities employing these technologies are in operation, which means a very low production (Figure 14). [27]

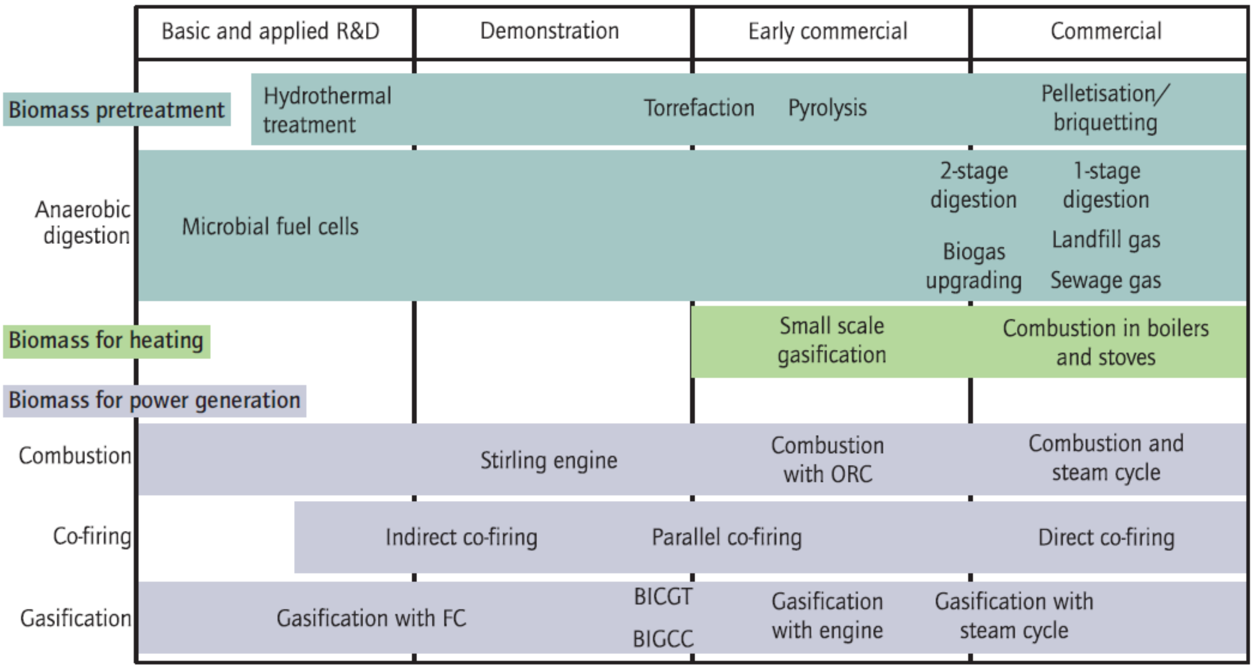


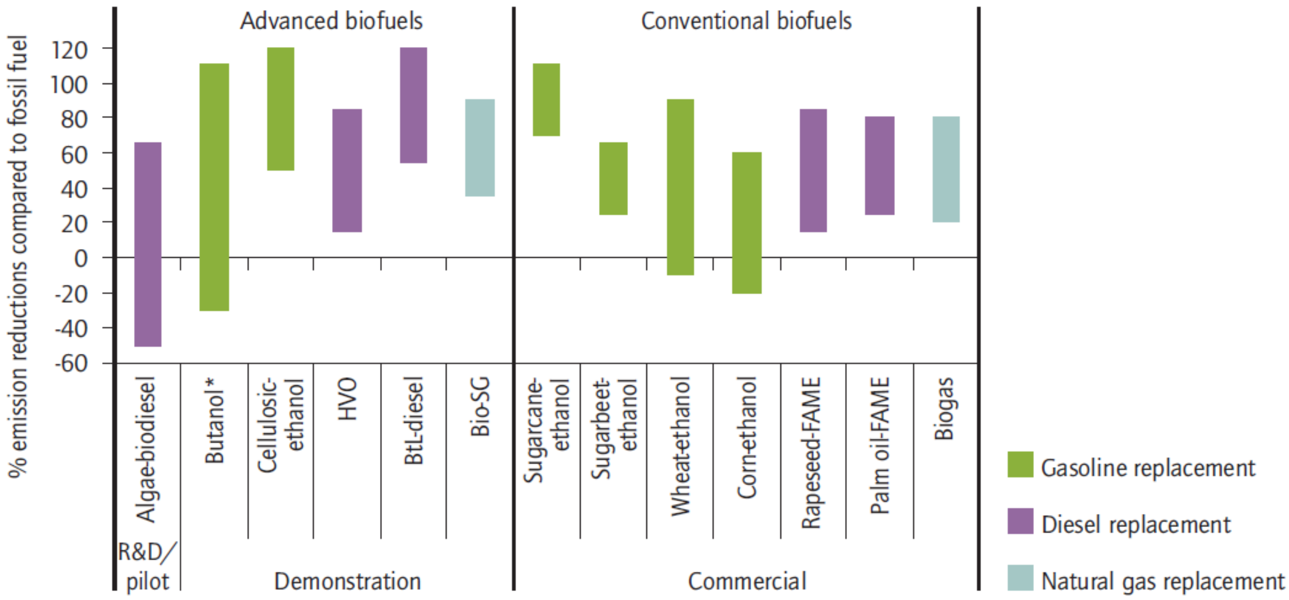
Figure 14: Overview of conversion technologies and their current development status [27]

Until now there are barriers for advanced biofuels before they can realize their potential to reduce GHG emissions. These include the following [28]:

- high cost of production;
- logistics and supply chain challenges;
- industry and consumer acceptance of biofuel quality;
- perceived risky investments;

- agricultural/forestry sector changes are needed to supply the biomass;
- misunderstanding of environmental / energy tradeoffs.

In general, it is necessary to make a whole life cycle analysis (LCA) to see the impacts of biofuels. Figure 15 shows different LCA (well-to-wheel) studies that compare the GHG emissions associated with different biofuels against the replaced conventional fuels. In the figure, a large range for each biofuel is shown, the reason is different feedstock production ways (including the amount of fertilizers) and manufacturing processes. The graphic covers mature, emerging and innovative processes. [23]



Note: The assessments exclude emissions from indirect land-use change. Emission savings of more than 100% are possible through use of co-products. Bio-SG = bio-synthetic gas; BtL = biomass-to-liquids; FAME = fatty acid methyl esthers; HVO = hydrotreated vegetable oil.
Source: IEA analysis based on UNEP and IEA review of 60 LCA studies, published in OECD, 2008; IEA, 2009; DBFZ, 2009.

Figure 15: Life cycle GHG balance of different conventional and advanced biofuels, and current state of technology [23]

2.4 Thermochemical conversion

Thermochemical biomass processing uses heat and catalysts to transform plant polymers into fuels, chemicals or electric power. Biochemical processes, which use enzymes and microorganisms for the same purpose, are the other option for biomass conversion. A comparison of biochemical and thermochemical processes is given in Table 3; it illustrates the advantages of thermochemical conversion [14]. Other benefits are the ability to produce different oxygenated and hydrocarbon fuels, shorter reactions times, lower cost of catalysts, and catalyst recycle. This is a very general comparison and different processes may cause slightly different results. [29]

Table 3: Advantages of biomass thermochemical conversion over biological/biochemical processes [14]

Thermochemical	Biological/biochemical
Effectively applied to almost any biomass feedstock.	Involves the use of microbes, enzymes, and/or chemicals to utilize the limited range of biomass
Relatively higher productivity (production per unit time) due to completely chemical nature of reaction.	Productivity is limited due to biological conversion. Increase would require higher capital investment such as bigger reactor
Multiple high-value products possible using fractional separation of products.	Normally, limited to one or few products and would require additional microbial culture, enzymes for more products
Independent of climate conditions, operates at much higher temperature range, therefore, effect of ambient temperature will be minimal	Mostly susceptible to ambient temperature, and so forth such as anaerobic digester, sunlight for algae ponds
Mostly complete utilization of the waste/biomass	Production of secondary wastes such as biomass sludge

There are three main processes of thermochemical biomass conversion and two lesser used options. The conversion routes for the intermediate energy carriers with the final resulting products are illustrated in Figure 16. [29]

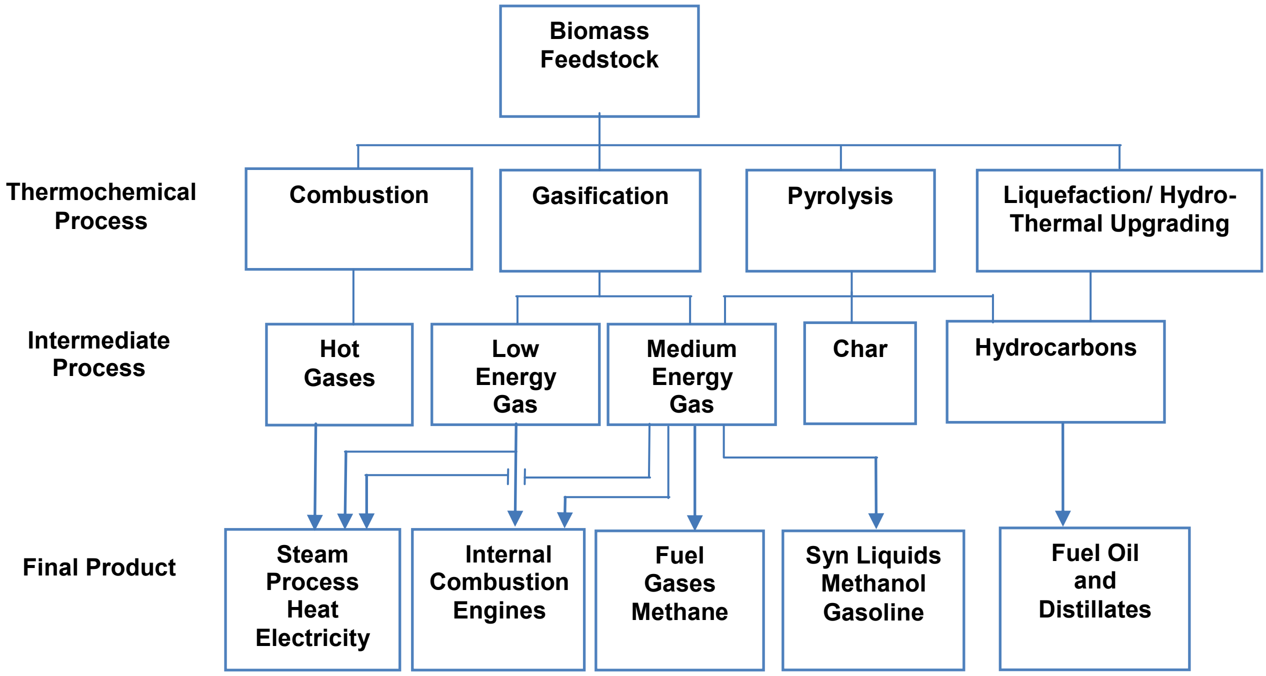


Figure 16: Main processes, intermediate energy carriers and final energy products from the thermochemical conversion of biomass [29]

a) Combustion

More or less quarter of a million years ago humans first learned to manage the fire; since that fuel burning was responsible for the development of the different societies. Combustion is defined as a rapid exothermic chemical reaction of fuel (for example, biomass) and oxygen to obtain thermal energy and flue gas (mainly, carbon dioxide and water). The reaction depends on a lot of factors like heating value and feedstock moisture, the amount of air for burning, and the construction of the furnace whereby flame temperatures can exceed 1650 °C. This technology is used since a long time, what is also the big advantage of direct combustion: a commercially well-developed and proofed technology. It is the basis for much of electric power generation around the world. [30]

The simplest combustion technology is a furnace, where biomass burns in a combustion chamber. In this process the organic compounds are converted into heat energy. Biomass can be represented as $C_xH_yO_z$ and the overall **combustion reaction** can be written as [30]:

$$\mathbf{C_xH_yO_z + (x + 0.25y + 0.5z)O_2 \rightarrow xCO_2 + (0.5y)H_2O}$$

The wood combustion can be divided in the following phases [30]:

1. Drying: water inside the wood boils off
2. Degasification: gas content is freed from the wood
3. Gasification: conversion of organic material to combustible gases under reducing conditions
4. Combustion: the rest of the wood (mostly carbon) burns
5. Post-combustion reactions with oxygen to CO_2 and H_2O

In industrial combustion, surplus air is supplied in addition to the theoretical amount ($\lambda=1$) required for biomass combustion. If too much air is added, a decrease in combustion temperature and thermal efficiency is the result. An overview of different combustion types with the features of each method is shown in Table 4 [7]:

Table 4: Biomass combustion type and features [7]

Combustion method	Combustion type	Features
Fixed bed combustion	Horizontal/Inclined grate Water cooling grate or air cooling grate Dumping grate	Grate is level or sloping. Ignites and burns as surface combustion of biomass supplied to grate. Used in small-scale batch furnace for biomass containing little ash.
Moving bed combustion	Forward moving grate Reverse moving grate	Grate moves gradually and is divided into combustion zone and after combustion zone. Due to continuous ash discharge, grate load is

	Step grate Louver grate	large. The combustion obstruction caused by ash can be avoided. It is possible to be applied to wide range of fuels from chip type to block type.
Fluidized bed combustion	Bubbling (stationary) fluidized bed combustion Circulation fluidized bed combustion	Uses sand for bed material, keeps fuel and sand in a furnace in boiling state with high-pressure combustion air, and burns through thermal storage and heat transmission effect of sand. Suitable for high moisture fuel or low grade fuel.
Rotary hearth furnace combustion	Kiln furnace	Used for combustion of high moisture fuel such as liquid organic sludge and food residue, or large waste etc. Restricted to fuel size on its fluidity. Suitable for hazardous waste combustion (T > 1200 °C)
Burner combustion	Burner	Burns wood powder and fine powder such as bagasse pith by burners, same as that for liquid fuel.

Co-firing must be mentioned here and refers to the technology where biomass is fired together with fossil fuels in the same power plant. The advantage is that by simply making some small changes or modifications to enable biomass treatment to an existing process, it becomes possible to fire organic material in highly efficient large-scale facilities. [7]

Direct combustion processes, especially with solid fuels, have some negative environmental impacts. The utilization of biomass like biofuels can avoid these harmful effects. Disadvantages are including an usually low efficiency (especially, the combustion of wood in traditional fireplaces/stoves) and the release of unburned hydrocarbons, which leads to poor air quality, secondary pollution and undesired health impacts. These effects can be worsened by the heterogeneous composition of waste biomass leading to unacceptable consequences. [31]

b) Gasification

The conversion of organic material to combustible gases under reducing conditions is called gasification. The oxygen is added in sub-stoichiometric amounts compared to the theoretical amount needed for a complete combustion. The oxygen can be added directly, using partial exothermic oxidation reactions for the production of the necessary gasification energy, or external heat is added (indirect gasification) in the absence of oxygen. In both methods, water in form of steam can be admitted to promote the production of hydrogen via the **water-gas shift reaction**. The gasification process is very flexible and makes the process attractive as a different solution. The options are presented in Figure 17 and include thermal power generation, hydrogen production and synthesis of fuels and chemicals. This also offers the prospect of combined refineries for the production of a mix of energy and chemical products. [8]

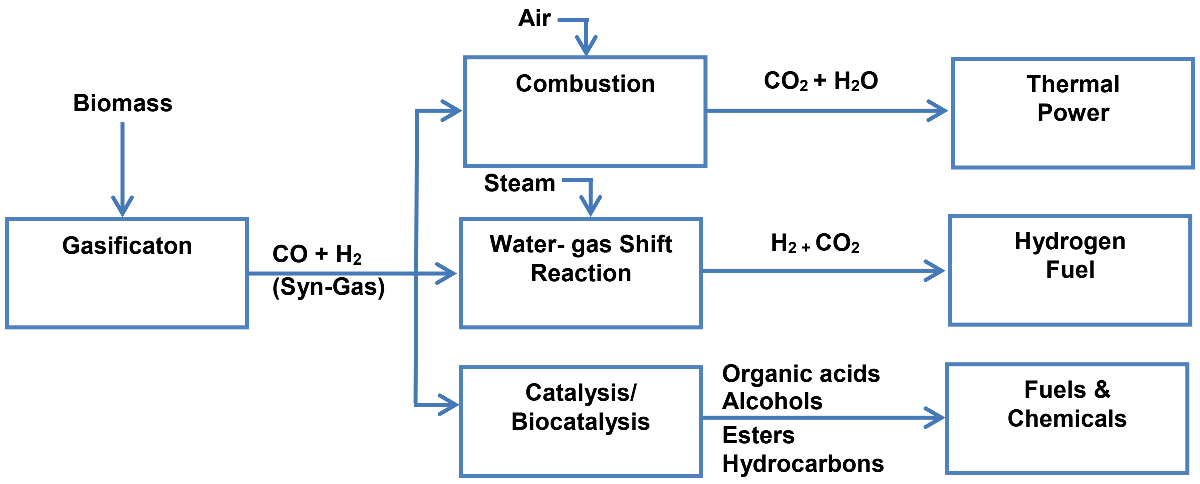


Figure 17: Gasification offers several options for processing biomass into power, chemicals, and fuels [8]

The different gasification methods can be classified according to a combination of the conditional factors presented in Table 5 [7].

Table 5: Gasification methods classification [7]

Classification	Conditional factor
Gasification pressure	• Normal pressure (0.1 – 0.12 MPa) • High pressure (0.5 – 2.5 MPa)
Gasification temperature	• Low temperature (≤ 700°C) • High temperature (≥ 700 °C) • High temperature decomposition (ash fusion point and above)
Gasification agent	• Air, oxygen, steam and different combinations of them • Carbon dioxide for particular time
Heating	• Direct gasification (internal loading) • Indirect gasification (external loading)
Gasifier types	Fixed bed, flow bed, circulating bed, entrained bed, mixing bed, rotary kiln, twin tower and molten furnace.

The following processes are occurring during the gasification [7]:

- Evaporation of surface moisture (until 100 °C).
- Evaporation of inherent moisture (110 -120 °C).
- Volatilization (200 – 300 °C):
  Thermal decomposition of biomass begins and CO, CO_2, H_2 and H_2O are vaporized as gas.
- Volatilization and gasification reaction:
  During the volatilization, the temperature raises and the volatile matter of hydrocarbons is transformed into heavy C_xH_y compounds. They are reacting with the gasifying agent and transform into light weight molecule gas. The formation of tar and soot is possible.
- Char gasification:
  The fixed carbon and ash in the biomass become char during the process while being heated to the surrounding temperature. The following reaction with the steam agent transforms CO into CO_2. If a surplus of steam is available and the temperature is over 750°C, a wet gas reaction occurs and produces a gas composed mainly of CO, CO_2, and H_2.

c) Hydrothermal processing

There are two main processes within this group: **hydrothermal liquefaction** (also known as direct liquefaction) and **wet gasification**. In general, this technology refers to biomass processing in water slurries (for wet biomass materials without drying) at elevated temperature and pressure to facilitate the chemical conversion processes. Typical parameters for this process are temperatures of 523 – 647 K and pressures from 4 to 22 MPa. At these temperatures, pyrolytic mechanisms in the biopolymers can be initiated whereby the pressure is necessary to maintain the water in a liquid phase. A big advantage of hydrothermal processes is that the hot water can serve as a solvent, a reactant and even a catalyst or catalyst precursor. Normally, the biomass compounds are not water soluble, but within the process parameters many organic compounds have a very high solubility. The advantage, that wet biomass can be used in the process and so a drying process can be avoided makes biomass gasification in supercritical water a promising technology. Examples show that **super critical water gasification of biomass** with at least 30 % of moisture needs less energy than drying it. The main reason is that the process saves energy necessary for the phase change from liquid to vapor. It is also possible to use the hot reactor effluent steam to preheat the feed stream. All these facts show that hydrothermal processes have a highly energy efficiency. [8] [30]

Hydrothermal liquefaction is biomass transformation into liquid fuels and chemicals by processing in a hot pressurized water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components. Until now, this technology has only been used in small scale research plants for short time periods. Over the time different processes have been developed. [30]

A generalized conceptual flow sheet for liquefaction is shown in Figure 18. [29]

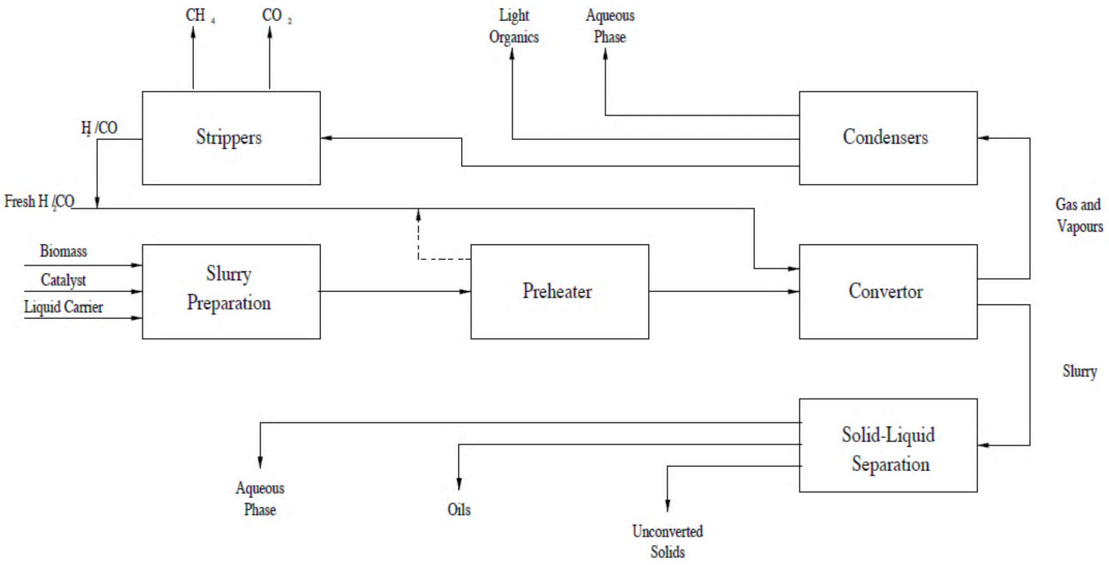


Figure 18: Flow sheet for liquefaction. [29]

Hydrothermal gasification (or wet gasification) is a process by which wet biomass can be gasified at low temperatures (300 – 400 °C) to make primarily CH_4 or at higher temperatures (600 – 700 °C) to make primarily H_2. In general, it is a highly efficient and economically attractive technology for biomass and waste valorization with a high reaction rate. [8] In this process the temperature can have different effects according to three identified regions [30]:

- Region I (773 – 973K supercritical water) – biomass decomposes and activated carbon catalyst is used to avoid char formation.
- Region II (647 – 773 K, supercritical water) – biomass hydrolyzes and metal catalysts facilitate gasification.
- Region III (below 647 K, subcritical water) – biomass hydrolysis is slow and catalysts are required for gas formation.

In summary, it can be said that **hydrothermal liquefaction and gasification** can be accomplished with careful management of time, temperature and pressure and the potential use of a catalyst. From the technical point of view, the process is manageable, but there are still parts which need to be developed, for example, mineral components control and water and nutrients recycling. Also, it is a promising technology; but a commercial plant for long term operation would be complicated and expensive to build and operate. [30]

d) Pyrolysis of biomass

This technology is described in detail in Chapter 4.

3 Specific Situation in Peru

Peru is a megadiverse country in a constant economic growth that urgently demands careful sustainable development to protect and preserve its natural wealth. The territory is located in tropical and subtropical South America. This would draw the conclusion that the climate should be warm and humid, but because of the presence of the Andes and a complex system of ocean currents and air masses movements, a rich variety of climates is generated (South Pacific Anticyclone). So, connected to its geological and ecological features, Peru becomes a megadiverse country. [32]

According to Pulgar Vidal (1940), Peru has 8 different terrestrial regions (*Chala, Yunga, Quechua, Suni, Puna, Janca, RupaRupa* and *Omagua*) and one maritimal region (*Mar Peruano*). However, the land could be broadly divided in 3 large regions: an arid desertic region (***Costa***) followed by the mountains (***Sierra***) and the tropical forest (***Selva***) into which those proposed by Pulgar Vidal can be included. On the other hand, 84 different Holdridge life zones can be found in Peru, the country with the largest amount (Figure 19) in the world. Only in the Peruvian Amazon exist around 1,700 varieties of birds as well as many species of mammals, fishes and insects, forming a great variety of unique fauna. Besides, the Peruvian flora has the greatest variety of domesticated plants in the world, for example, there are over a thousand varieties of potatoes. All these facts make Peru one of the countries with the highest natural variety in which nearly all kinds of ecological zones can be found. [32]

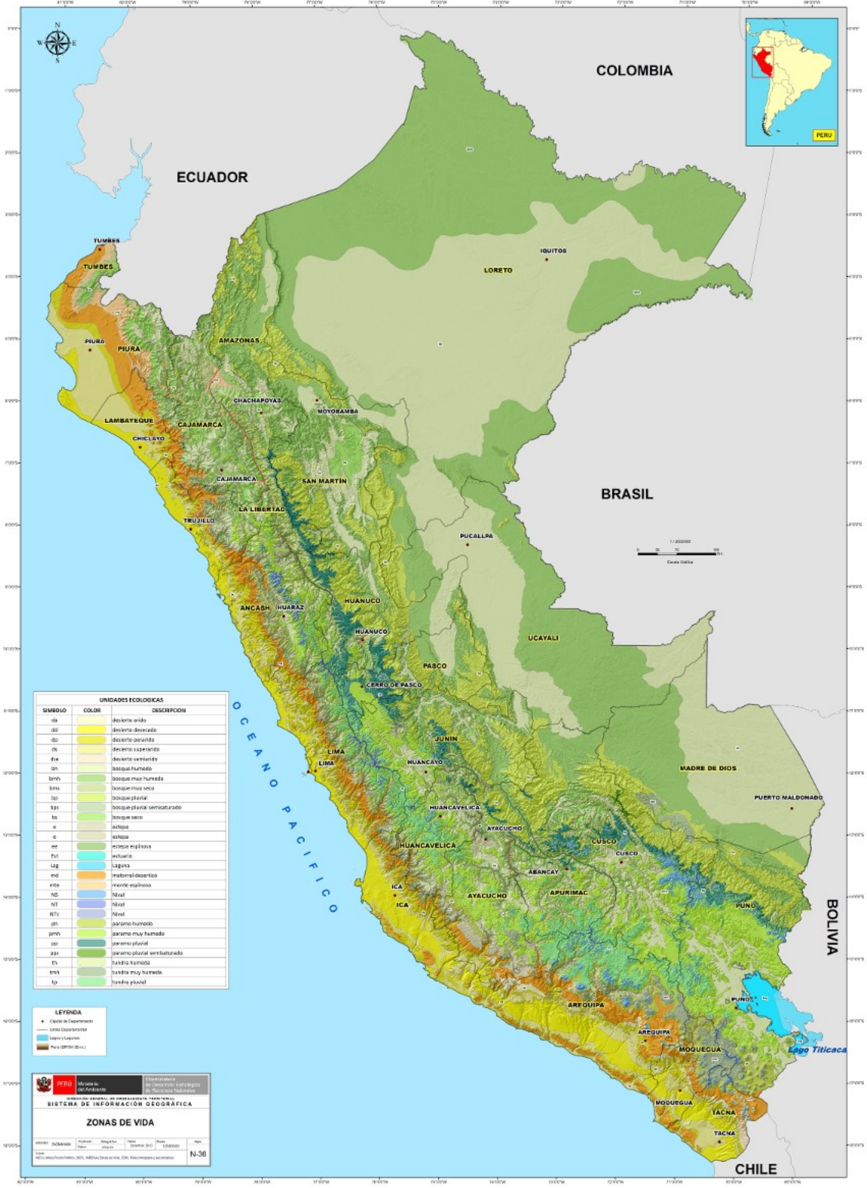


Figure 19: Life zones in Peru [32]

Out of a total area of 128,521,560 ha, the area dedicated to agriculture is roughly 24 percent of the total land, and the forests cover 70 percent of the national territory, including the tropical rainforest. With nearly 36,000,000 ha the mountainous area, called ***Sierra*** compromises one third of the Peruvian country. The third biggest region, after the rainforest and the mountainous area, is the coast which covers only 15,087,282 ha. [33] Peru has 29,399,817 inhabitants according to the World Bank 2011 [34]. Connecting these data with the population statistics, the results show that in the coastal strip (7.5 % of the country area) lives 54.6% of the Peruvians, in the highlands - which represents one third of the country – 32 % of the population is living and in the biggest natural region of Peru - which represents 62 % of the land - only live 13.4 % of the inhabitants. [35]

The economy of this developing country has grown 6.92 % p.a. in the year 2011 with the mining sector as the most important income. [36] About 91.5 % of the Peruvians living in urban areas have access to public water systems compared to only 52.3 % in rural zones. It is also a fact that no more than 72.5 % of rural households have electric lighting in comparison to 98.8 % of urban ones. Another alarming figure shows that 34.7 % of the population suffers from malnutrition (23.9 % in Lima and up to 48.9 % in rural zones), and 13.9 % of the children younger than 5 years are affected by chronic underfeeding. These numbers show that Peru is in a state of food insecurity and, for this reason, it must be avoided that food production is affected by the bioenergy industry. It is important to mention that the lack of food and the rise of food prices are not only linked to liquid biofuels production, these are also associated with low levels of income, inadequate use of food and other multiple factors. [37] In October 2012, 167 social conflicts in Peru were registered, 66 of them were latent and over 63 % of the total were social-environmental conflicts, in most cases caused by mining activity. [38]

The total energy demand in Peru amounts to 638,190 TJ and is covered by following sources [39]:

- 46 % of oil and NGL (Natural Gas Liquids),
- 23 % natural gas,
- 15 % biomass,
- 11% hydropower,
- and 5 % of coal.

The highest energy consumption of 40 % has the transport sector, where the consumption of petroleum products represents 94 % and natural gas reaches a share of 6 %. Solar energy and wind energy, with no more than 300 TJ, are playing only a very minor role in Peru's energy matrix until now. The aim of the Peruvian government is to increase the share of renewable energy up to 33 % until 2030. According to Supreme Decree No. 064-2010-EM, the main objectives for the “NATIONAL ENERGY POLICY OF PERU 2010-2040” are:

1. Count on a diversified energy mix, with emphasis on renewable energy resources and energy efficiency.
2. Count on a competitive energy supply.
3. Achieve self-sufficiency in energy production.
4. Develop an energy sector with minimal environmental impact and low carbon emissions in a sustainable development framework.
5. Strengthen the institutional framework of the energy sector.

For this purpose the government began to create legal frameworks to raise the production and use of renewable energies. For example, normal fuels have to be mixed compulsory with biofuels. The law demands an additive of [39]:

- 5 % biodiesel in diesel since 2011, and
- 7.8 % ethanol in gasoline since 2010.

Until now, this demand is fulfilled in Peru with first generation biofuels leading to the before mentioned problems (see chapter 2.3.1).

The total offer of available biomass in Peru for the production of energy is about 272 million metric tons according to WISDOM (Wood fuels Integrated Supply/Demand Overview Mapping) analysis carried out by FAO (2010). This number consists of 16 million tons of organic waste available yearly from agricultural and forest industries. The remaining 256 tons represent the potential of woody biomass from the natural forests of Peru. The tropical zone has the biggest amount of available forest biomass, while the arid costal region and the south of the Sierra have only a short supply. This heterogeneous distribution of resources is the result of geographical and climatic variability that characterizes the Peruvian territory. But the results of the WISDOW analysis in Peru show that many regions of this country have important volumes of biomass that could potentially be used to provide locally generated energy. For example, the woody biomass and residues from the forest industry could be used for direct or indirect local production of energy and fuel, but also be transported like briquettes, coal, gas, within others, over long distances. [40]

The generation potential data for renewable energies in Peru expressed in tons of oil equivalent (Toe) is shown in Table 6. [41]

Table 6: Renewable energy production potential in Peru (*i.e.* assessments by authorities) [41]

Source	**Generation Potential**
Hydroenergy	2,852,000 Toe/year
Fuel wood	66,000,000 Toe/year
Agricultural waters	530,000 Toe/year
Livestock wastes	150,000 Toe/year

Agro industrial wastes	395,000 Toe/year
Urban waste	236,000 Toe/year
Wind power	450 – 5,000 kWh/m^2/year
Solar	4 - 5 kWh/m^2

Life cycle analyses of biofuel production in the Peruvian Amazon are showing that not all production ways make environmental sense. Different scenarios show that the answer of the question if biofuels are ecological or not depend strongly on the previous land use of the area where the energy crops are planted. The most harmful scenarios are those where primary forests are destroyed to get farmland for the energy crops. [17]

This can be shown with the calculated carbon debt of 8 different scenarios during the research of SNV. Positive environmental impact have oil palm and jatropha crops on degraded forest land with values of – 8.1 and - 9.5 tCO_2eq / ha, while biofuel production in primary forest incurs debts (the amount of years necessary using biodiesel, in order to compensate for the carbon emissions caused by the land use change to produce biodiesel) of 40 and 140 years for oil palm and jatropha, respectively. [17]

There are some projects in Peru in the field of renewable energy going on. Sugar cane, for example, is used for the production of ethanol. Peru counts on 12 refineries with a potential production capacity of 64 million liters per year. The high water demand of sugar cane and the water constraints in some regions of Peru raise the question, if it is more important to grow agro-biofuels or crops for food production. It seems that for the biodiesel production, oil palm and jatropha are the most potential feedstock. A small number of projects with jatropha are at experimental stage. In the other hand, there is an installed area of more than 44,882 ha for oil palm whereby 38 % of the total area is in production, 34 % in growth and the rest in nurseries. [40]

The most common bioenergy types used in Peru are solid biofuels like dung, firewood and charcoal; 10 – 12 % of total energy consumption is based on solid biomass. For the generation of electric power, the most important bioenergy resource is biogas generated by the anaerobic decomposition of plant and animal wastes. Residues materials used include sugarcane bagasse, rice husk, forestry waste, wheat chaff, and rests from the poultry, beef cattle and pigs production. From January 2012 to September 2012, 114.9 GWh of electricity were produced by biogas, nearly twice compared to the production in the same period in the year 2011. [42]

4 Basic principles of pyrolysis and fluidized bed reactors

Pyrolysis is thermal decomposition of organic material into a range of useful products, occurring in the total absence of oxygen or with a limited supply of oxidizing agents. It is always the first step in combustion and gasification processes followed by total or partial oxidation of the intermediate products. Basically, the large chains of hydrocarbon molecules of organic feedstock break down into a variety of smaller and simpler gaseous molecules (CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc.), liquid compounds (tars, heavier hydrocarbons, and water) and solids (mostly char or carbon). An example of this decomposition is shown in Figure 20. [43] [9]

The general equation for pyrolysis can be described as following:

$$\underset{\text{Biomass}}{\mathbf{(C_6H_{12}O_6)_m}} \xrightarrow{\textbf{Heat}} \underset{\text{Gas}}{\mathbf{(H_2 + CO + CH_4 + \ldots.. + C_5H_{12})}} + \underset{\text{Liquid}}{\mathbf{(H_2O + CH_3OH + CH_3COOH + ..)}} + \underset{\text{Char}}{\mathbf{C}}$$

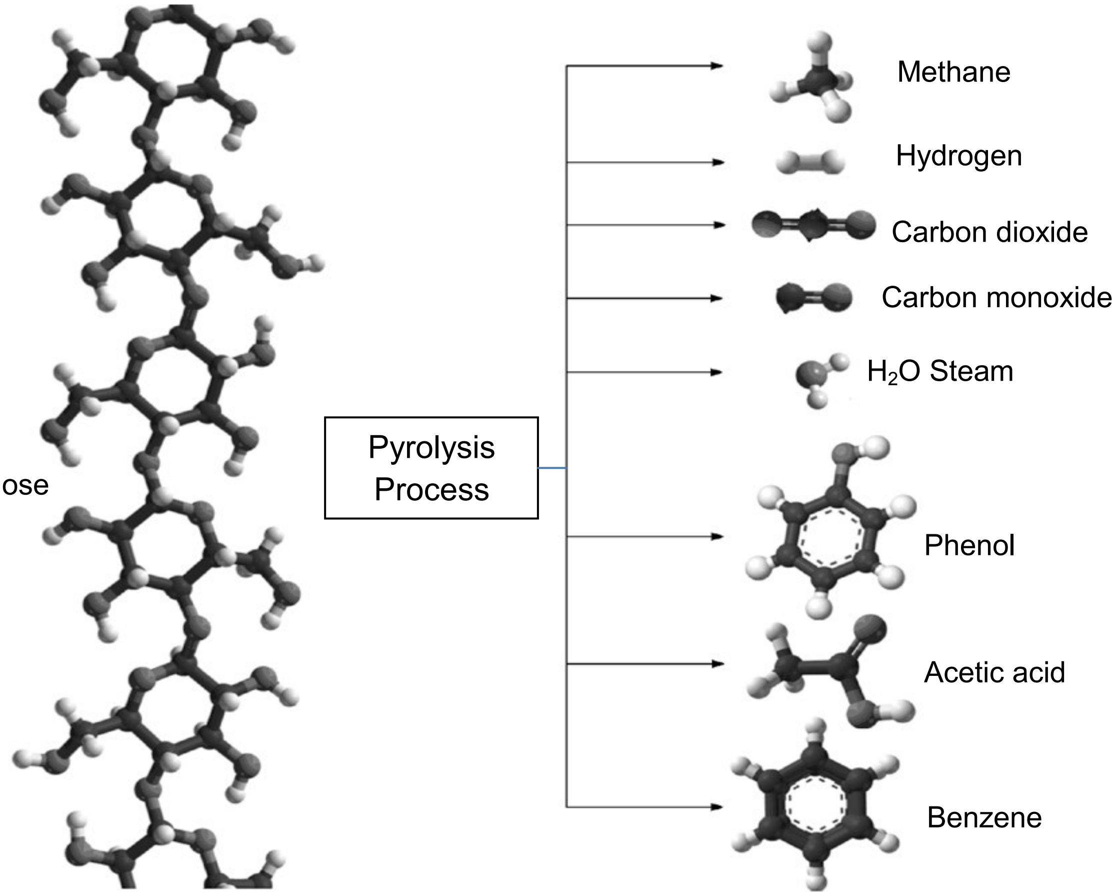


Figure 20: Decomposition process of large hydrocarbon molecules during pyrolysis. [9]

Figure 21 shows a schematic pattern of biomass decomposition in a pyrolysis process of wheat straw [6].

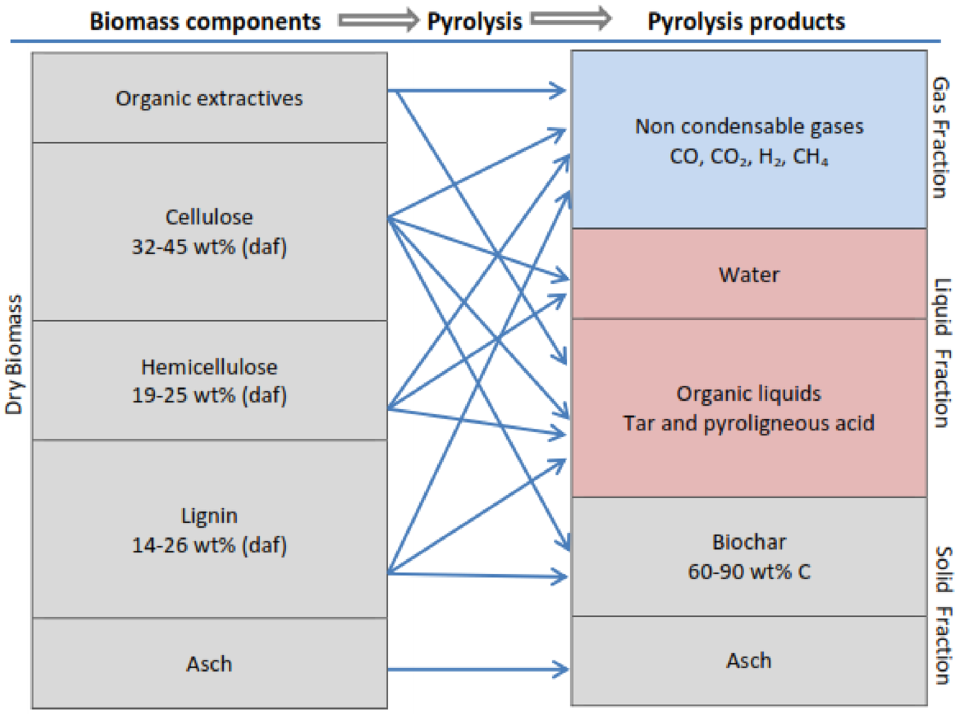


Figure 21: Generalized biomass thermal decomposition pattern by pyrolysis process [6]

The pyrolysis of a particle is illustrated in Figure 22. The high temperature in the reactor is transferred from the bulk to the particle by convection and the heat is conducted from the particle surface toward to the particle center. During the process, volatiles are produced and diffuse to the particle surface whereby the char remains as the constituent of the layer. Condensable gases break down further into non-condensable gases (CO_2, H_2, CO and CH_4), or liquids. Decomposition partly occurs through heterogeneous gas-solid phase and homogeneous gas phase thermal reactions. Lower process temperature and longer vapor residence times favor charcoal production. High temperature and longer residence time increase the biomass conversion to gas, but **moderate temperature and short vapor residence time are optimum conditions for liquids production**. The nature of products and yield distribution depend on several factors, including pyrolyzer design , biomass physical and chemical characteristics , pyrolysis temperature, heating rate, and gas flow (resident time), within others. [9]

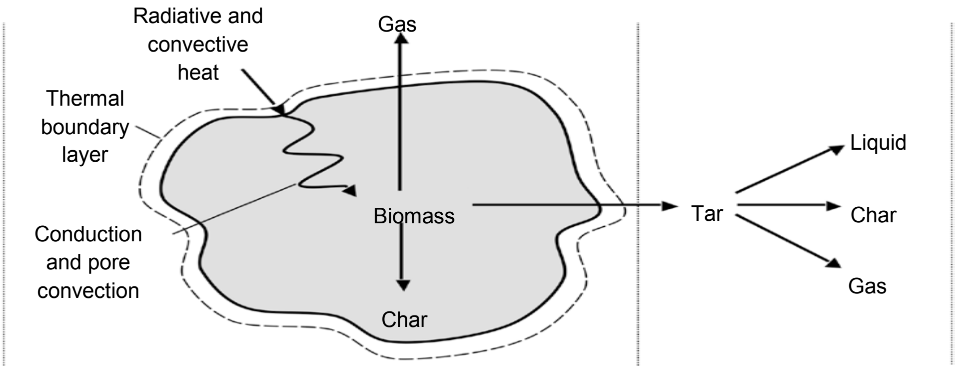


Figure 22: Pyrolysis in a biomass particle. [9]

The use of pyrolysis products leads at least to a closed carbon cycle but, if char from the pyrolysis process is used like fertilizer, the result would be a negative carbon cycle. This carbon-negative bioenergy production process is shown in Figure 23. [44]

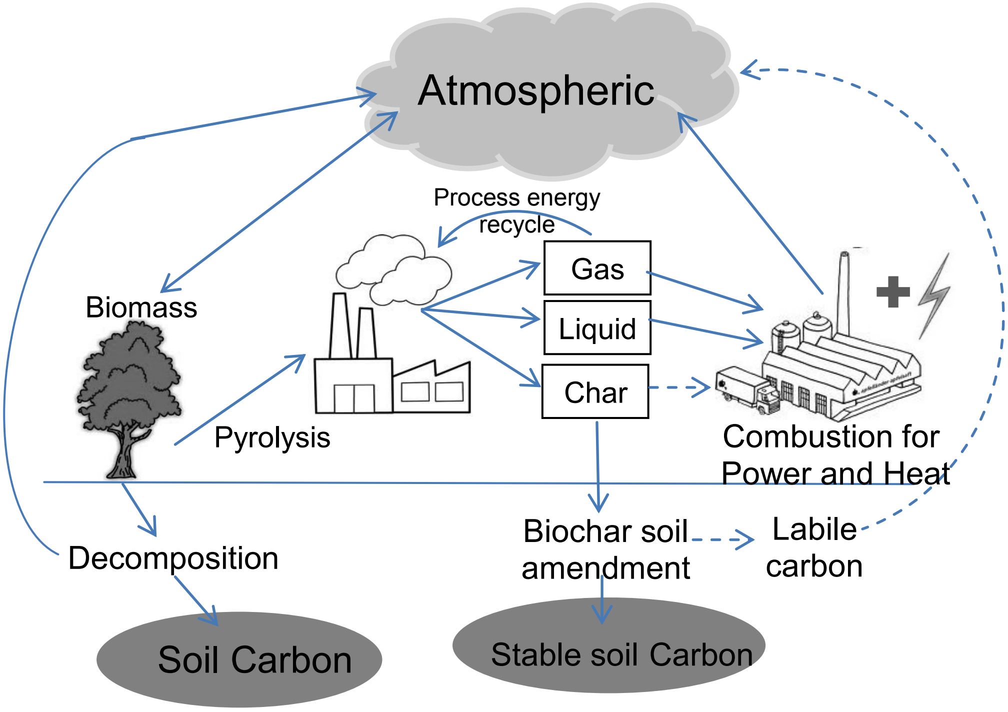
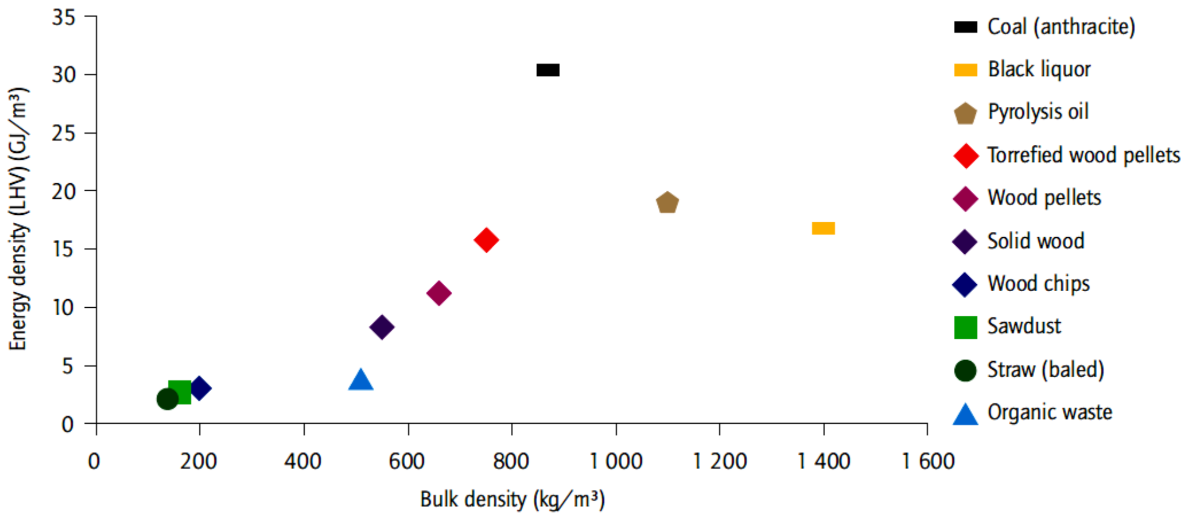


Figure 23: Scheme showing main carbon flows associated with biomass pyrolysis [44]

Another proposal for closed carbon cycle is the full combustion of biomass combined with carbon capture and storage technology. [6] [44]

Fast pyrolysis for liquid fuel production is of particular interest as liquids are transportable and easy to store due to the good energy to bulk density relationship (Figure 24) [27]. [43]



Source: IEA analysis based on DENA, 2011; FNR, 2011a; IEA Bioenergy, 2011; Kankkunen and Miikkulainen, 2003. For detailed data see Table 6 in Appendix I.

Figure 24: Comparison of bulk density and energy density [27]

4.1 Types of pyrolysis technologies

The pyrolysis processes can be divided into several subcategories, depending on design and operation conditions. A basic classification of pyrolysis processes, including a distribution of mass percentage on products, is presented in Table 7 [8]. [45]

Table 7: Typical product yields obtained by different pyrolysis modes with wood [8]

Mode	Liquid (bio-oil)	Solid (biochar)	Gas (process gas)
FAST Moderate temperature (~ 500 °C) Short vapour residence time (~ 1s)	75 % (25 % water)	12 %	13 %
INTERMEDIATE Low-moderate temperature (~ 500 °C) Moderate hot vapour residence time (~ 10 – 30 s)	50 % (50 % water)	25 %	25 %
SLOW TORREFACTION Low-moderate temperature(~ 290 °C), solids residence time (~ 30 min)	0 % (if vapours are burned)	80 %	20 %
SLOW CARBONIZATION Low-moderate temperature(~ 400 °C), Long residence time (hours → days)	30	35 %	35 %

GASIFICATION high temperature (~ 750 - 900 °C)	5 % (5 % water)	10%	85 %

Pyrolyzers are in use since humans have begun to produce charcoal. The first pyrolyzers operated in batch mode, had a very slow heating rate and very long reaction times to produce a maximum of char. Today a variety of different pyrolyzers are in use. According to the heating rate, the peak pyrolysis temperature, residence time, feedstock and expected yields of the products, an appropriate technology has to be chosen. Basically, they can be classified into fixed bed, fluidized bed, and entrained bed referred to the gas-solid contacting mode. Furthermore, they can be subdivided depending on design configuration. The most common designs in use are [9] [46]:

- Fixed or moving bed
- Bubbling fluidized bed
- Circulating fluidized bed
- Ultra-rapid
- Rotating cone
- Ablative
- Vacuum
- Auger

The main types of pyrolysis reactors are briefly described below:

Bubbling bed pyrolyzers have a hot sand bed fluidized by an inert gas stream (for example: N_2, recycled flue gas, etc.). Fluidization is a process where a fluid is passing through a granular material (for example, sand), whereby the granular material is converted from a solid-like state to a fluid-like dynamic state. When crushed biomass (>2 mm) is fed into the hot sand bed, it comes to an intense mixing and a high and quick heat transfer to the organic particles. The solid granular also provides a good and uniform control of the temperature. In Figure 25*,* a bubbling fluidized bed (a) and a circulating fluidized bed (b) pyrolyzer are shown. Both are working on the same principle, only the circulating fluidized bed is working in a special hydrodynamic regime (fast bed) which is highly expanded and the solids are removed and recycled continuously. The fast bed offers a better temperature control with a higher superficial gas velocity. This allows a large throughput from biomass and an excellent mixing of the particles. [9] [47]

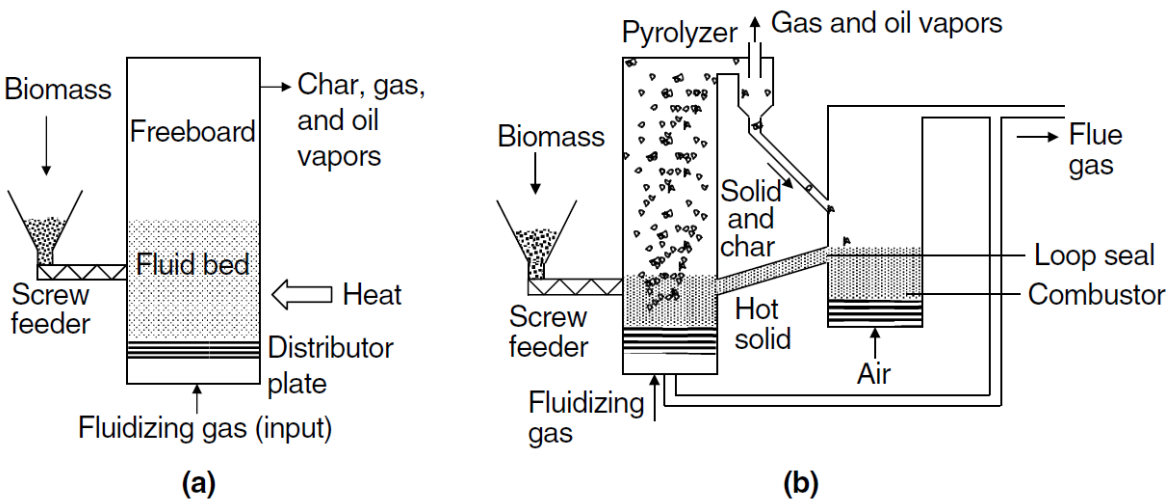


Figure 25: Simplified layout of a bubbling fluidized bed (a) and a circulating fluidized bed (b)pyrolyzer. [9]

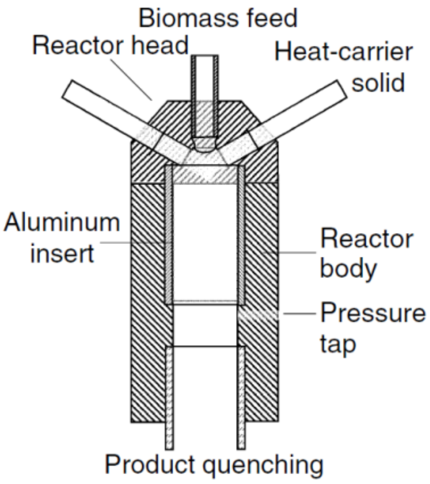


Figure 26: Layout of an Ultra-Rapid pyrolyzer [9]

Pyrolysis with **ultra-rapid pyrolyzer** (Figure 26) is a process with temperature of 650 °C to maximize the liquid yield or with 1,000 °C for a high gas production. The main characteristic of this process is an extremely fast mixing of the feedstock with a solid heat carrier and a short residence time. The heat transfer and the heating rate are very high. A rapid quenching of the first products occurs after the first reactions followed by a gas – solid separator to return the solid into the reactor. The heat is provided from a separate combustor. The non-condensable gases and primary product vapors come to separators of the gas liquid products. [9]

An **ablative pyrolyzer** (Figure 27) works with conduction heat transfer, which requires a good surface contact. Therefore, the biomass particle is pressed against the heated reactor wall with high pressure, so providing a much higher heating rate, inducing rapid melting and sublimation of the organic material. There are two options to create the pressure between the biomass and the wall, either by a mechanical system or by centrifugal force. The wall temperature is 600 °C. The biomass leaves a liquid film behind on the wall which evaporates and leaves the zone. The condensation and collection of the products proceed like in other pyrolysis processes. [9] [48]

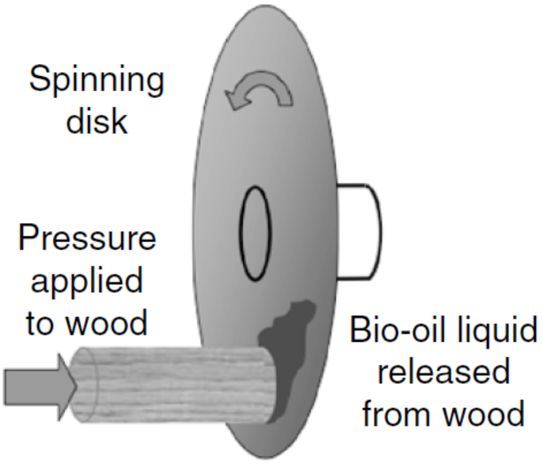


Figure 27: Layout of an ablative pyrolyzer. [9]

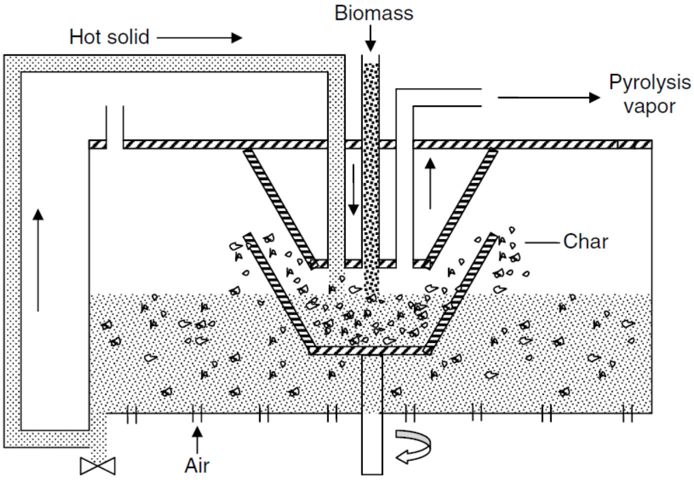


Figure 28: Rotating cone reactor [9]

A reactor with a **rotating cone pyrolyzer** (Figure 28) relies on the application of centrifugal forces on a mixture of hot sand and biomass particles. Biomass particles are fed to the centre (bottom) of a rotating cone reactor together with heated solid particles. The mixture is transported in spiral movements to the top of the reactor while centrifugal force pushes them against the hot wall. The heat transfer occurs by gas and solid phase convection and also by conduction with the hot wall. This allows a high heat transfer rate even in big reactors. The solid particles are continuously transported into a fluidized bed combustor and the reheated sand is returned to the pyrolyzer. Pyrolysis vapors are leaving through another tube at the top of the reactor. The char is burned and used to provide the process heat. Very short residence times are typical for the process. Another advantage of the process is that inert carrier gas is not necessary what is minimizing the dilution of volatile products. The complex geometry is a challenge for such a process. [9] [49]

A **vacuum pyrolyzer** (Figure 29) works under low pressure (0.15 – 0.20 atm) and moderate temperatures (400 – 500 °C). The biomass is not heated rapidly but the vacuum serves to decrease the resistance experienced by molecules diffusing. A vacuum pump is producing the low pressure and controls the residence time of volatiles. [48] [49]

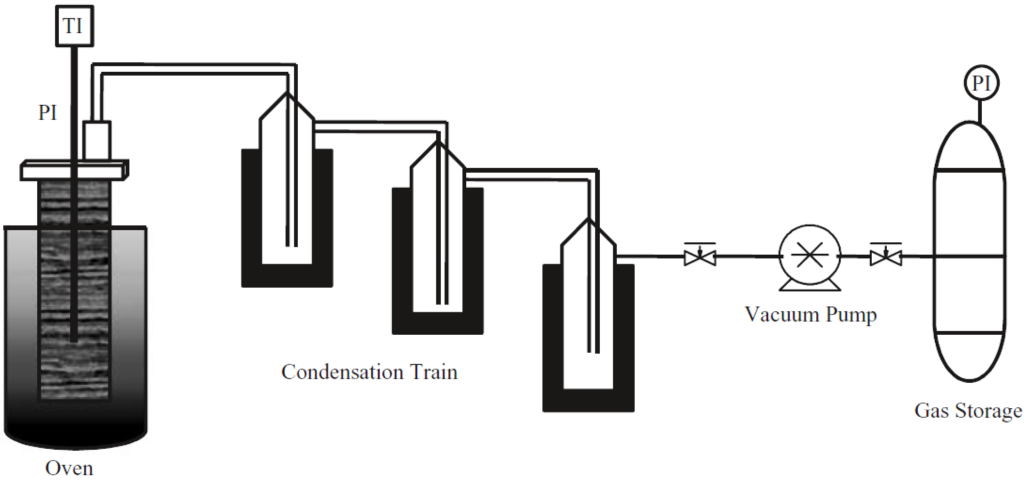


Figure 29: Scheme of a vacuum pyrolysis [48]

Produced vapors are only a very short time in the reactor which avoids secondary decomposition. Like in ablative pyrolysis process, no carrier gas is needed hence reducing the dilution of evolving gases. [48] [49]

Biomass particles are moved in an **auger pyrolyzer** (Figure 30) by using an auger (screw-type conveying) through a tube (400 – 800 °C). This tube can be heated externally or hot sand is co-fed with the biomass. The melting velocity increases with the pressure against the wall. It is a constantly working process in which the biomass is devolatilized and gasified without the use of carrier gas. In comparison to other reactors the energy costs are usually lower, but the mechanical system makes a scale up harder. There are also models with a twin-screw. [48] [49]

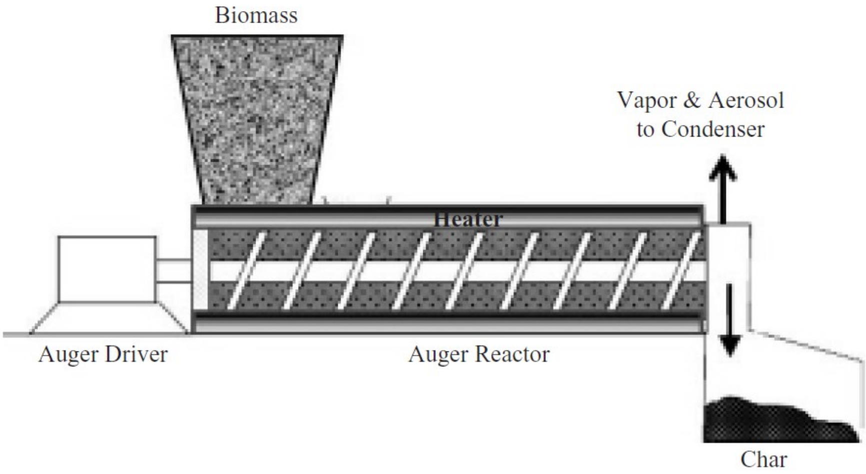


Figure 30: Scheme of an auger reactor. [48]

Table 8 presents a summary of fast pyrolysis reactor systems. It shows the key features of each reactor system and their development status. [46]

Table 8: Fast pyrolysis reactor characteristics overview for bio-oil production [46]

Property	Status[1]	Bio-oil yield on dry biomass [wt%]	Complexity	Feed size specification	Inert gas requirements	Specific reactor size	Scale up	Gas quality
Fluid bed	Com.	75	Medium	High	High	Medium	Easy	Low
CFB & Transported bed	Com.	75	High	High	High	Medium	Easy	Low
Rotating cone	Dem.	70	High	High	Low	Low	Medium	High
Entrained flow	Lab.	60	Medium	High	High	Medium	Easy	Low
Ablative	Lab.	75	High	Low	Low	Low	Difficult	High
Screw or Auger	Pilot	60	Medium	Medium	Low	Low	Medium	High
Vacuum	None	60	High	Low	Low	High	Difficult	Medium

Notes: 1) Com = commercial (2 t/h - 20 t/h); Dem = demonstration (200-2000 kg/h); pilot (20-200 kg/h); Lab = laboratory (1-20 kg/h); 2) Colors: green = favorable feature; purple = moderate feature; blue = unfavorable feature; CFB = Circulating Fluidized Bed.

4.2 Fast pyrolysis

The following definition and principles of fast pyrolysis from Bridgwater [50] are used in this work:

> *"In fast pyrolysis biomass decomposes to generate mostly vapors and aerosols and some charcoal. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yields of liquid. The essential features of a fast pyrolysis process for producing liquids are:*

- *very high heating and heat transfer rates at the reaction interface, which usually requires a finely ground biomass feed,*
- *carefully controlled pyrolysis reaction temperature of around 500 °C and vapor phase temperature of 400-450 °C,*
- *short vapor residence times of typically less than 2 seconds, and*
- *rapid cooling of the pyrolysis vapors to give the bio-oil product."*

Some authors understand flash pyrolysis as fast pyrolysis, but for others a shorter residence time and a little bit lower heating rates in the flash pyrolysis process are different. [8] [44] [9]

Fast pyrolysis occurs in a period of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes as well as phase transition phenomena play important roles. The critical issue is to bring the reacting biomass particle to the optimum process temperature and minimize its exposure to the intermediate (lower) temperatures that favors formation of charcoal. One way of reaching this goal is by using small particles, for example in fluidized bed processes. A very fast heat transfer is very important. The main methods for heat generation are shown in Figure 31, including transfer *via* reactor walls, gas and bed material (removing and reheating). [8] [51]

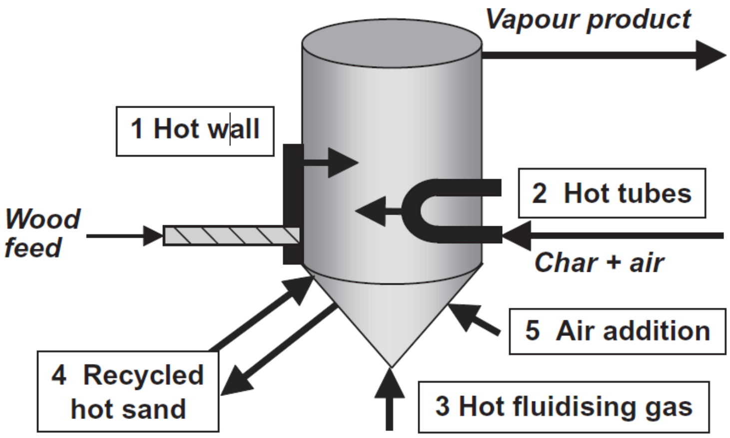


Figure 31: Methods for providing process heat to fast pyrolysis. [51]

A big advantage of fast pyrolysis is the fact that the process heat can be provided from the process byproducts gas or char, or from fresh biomass. [8]

Figure 32 shows a general flow sheet of a fast pyrolysis process, where the produced gas is used to power the necessary process heat. [48] [49]

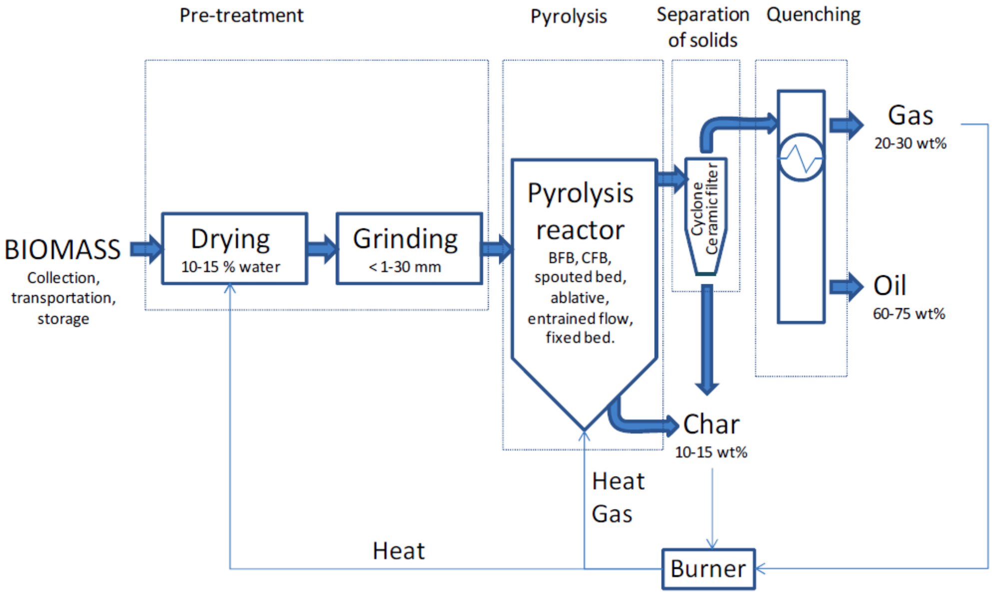


Figure 32: An example for a simplified layout of a fast pyrolysis plant. [49]

4.2.1 Fast pyrolysis kinetics

In general, it is quite difficult to get reliable kinetic rate constants data, which can be used for a variety of biomass and different heating rates. The kinetics are very complicated; on one hand, fast pyrolysis is a non-equilibrium and non-steady process and, on the other hand, there is the heterogeneous nature of the feedstock to be considered. For example, hemicelluloses, cellulose and lignin have their own different pyrolysis chemistry (chemical degradation kinetics of individual biomass components). Description of the different kinetics models and chemical reactions would fill a book, which is why in this work, for engineering purpose, only the simplified mechanism for the thermal degradation of biomass is presented. This **simplified mechanism** includes the following steps:

1. Degradation of biomass into primary products: tar, gases and char;
2. decomposition of primary tar and semi tar to secondary products,
3. and continuous interaction between primary gas and char.

4.2.2 Fast pyrolysis products

Four different chemically product groups are always generated in biomass pyrolytic decomposition, whereby their shares may vary greatly depending on the chosen process conditions under which the pyrolysis is carried out:

- An **organic liquid**, which consists mainly of oxygen-containing compounds,
- **water**, mixed or separated from the organic liquid depending of the characteristics of the liquid,
- a **gas** (mainly carbon dioxide (**CO_2**), carbon monoxide (**CO**) and methane (**CH_4**)).
- and **char** with ash fractions.

The main product, **bio-oil**, is obtained in yields of up to 75 wt% (in the most developed processes) on dry feed basis. Bio-oil is a liquid mixture of oxygenated compounds containing various functional chemical groups, such as carbonyl, carboxyl and phenol. The uses of bio-oil are very diverse and far reaching; some examples are given in Figure 33 [53]. [46]

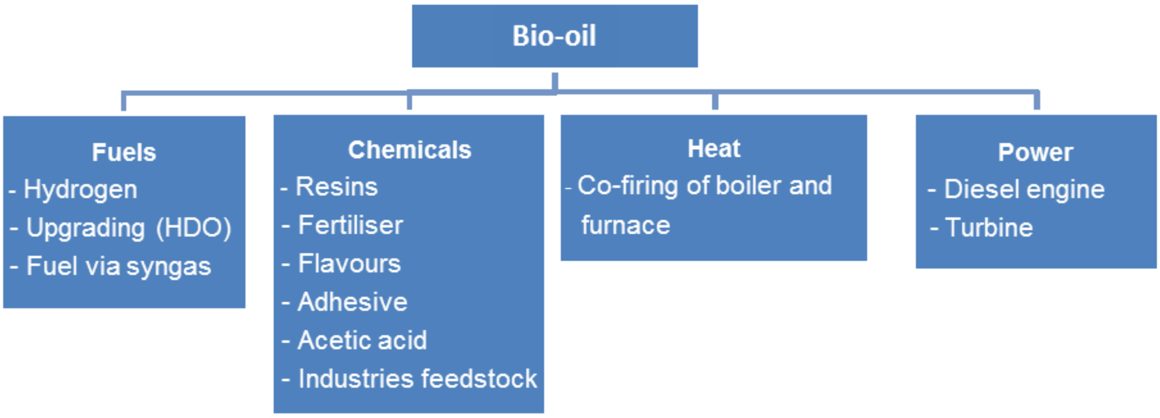


Figure 33: Different applications of pyrolysis bio-oil. [53]

Typical bio-oil properties are compared with normal fuels (light oil and heavy fuel oil) in Table 9. [47]

Table 9: Properties of bio-oil (from wood pyrolysis) compared with other fuels. [47]

Property	Bio-oil	Diesel fuel (No. 2)	Heavy fuel oil (No. 6)
C *(wt%)*	54 – 58	87.3	87.7
H *(wt%)*	5.5 – 7.0	12.0	10.3
O *(wt%)*	**35 – 40**	**0**	**1.2**
N *(wt%)*	0 – 0.2	<0.01	0.5
S *(wt%)*	0 – 0.04	0.1	0.8
Ash *(wt%)*	0 –0.2	<0.001	0.07
Higher heating value (MJ/kg)	16 – 19	46.7	41
Density (kg/liter)	1.2	0.86	0.94
Water content	15 – 30	--------	0.1
pH	2.5	--------	--------
Viscosity at 50◦C (mm2/s)	11 – 115	2.6	180
Solids (wt%)	0.2 – 1.0	--------	1

Pyrolysis gas yields in fast pyrolysis processes can range between 15 - 30 wt%, depending on the process parameters. Temperature and residence time have a strong influence on the gas production. There is also a wide variability in the gas composition. A typical composition may be: **CO (30 – 40 %), N_2 (0 – 60 %), CO_2 (20 – 25 %), H_2 (5 – 10 %) CH_4 (5 – 15 %)**, and the rest are C_2 – C_5 oxygenated and non-oxygenated organics. The gas normally is recycled for process energy (calorific value: 10 – 20 MJ/Nm^3) or to dry the feedstock. There are also investigations for other different applications, but this would bring higher technical and economic challenges. [49]

In the pyrolysis process, the thermal degradation of the biomass particles leaves behind a rigid amorphous carbon matrix referred to as **bio-char**. Depending on the process parameters, 10 to 35 % bio-char is produced. It has an amorphous structure and does not conduct electricity. The char can be used as fuel in boilers (calorific value 30 – 35 MJ/kg), as well as adsorbent and gasification feedstock. The incorporation of bio-char into agricultural soils is also proposed to reduce the greenhouse gases emissions and increase the agricultural productivity because it favors nutrient fixation and microbial activity. [46] [49]

4.3 Fast pyrolysis of biomass in fluidized bed reactors

A fast pyrolysis process includes feedstock drying to typically less than 10 % water in order to minimize water content in the product liquid oil. Feed grinding (≤ 2 mm in the case of fluid bed reactors) is needed in order to give sufficiently small particles to ensure rapid pyrolysis reactions. Virtually, any form of biomass can be considered for fast pyrolysis. The heart of a fast pyrolysis process is the **Fluidized Bed type reactor**, as in this work.

The advantages of a Fluidized Bed are [50] [47] [46]:

- excellent interactions between gas and goods (bed material),
- excellent heat transmission,
- excellent mass transport,
- a homogenous mixture in the reactor,
- easy to seal reactor because few moving parts.

However, there are also some disadvantages like erosion (the sand destroys the walls of the reactor), as well as the possibility that the sand of the bed escapes with the off gas, etc. One of the main features is, that the whole process only works without the presence of oxygen, otherwise incineration occurs. So, the reactor has to be airproof and also the entry of oxygen with the biomass has to be avoided. [52]

4.4 Turbulent Fluidized Bed

The fluidized bed can be formed as a gas-solid or liquid-solid fluidized bed based on the state of the flowing through fluid. However, only the gas-solid fluidized bed is here discussed. Fluidization, like heat transfer and all other chemical and physical processes in a pyrolysis reactor, is a very complex and wide-area topic. In this work only the basic principles to understand the process are discussed.

4.4.1 Solid particles – Geldart classification

The particles behavior in the fluidized bed depends mostly on particle sizes, densities and shapes (regular, spheres, squamous, fibrous, etc.) of the particles. Not every particle can be fluidized. Geldart made a careful observation of many sorts and sizes of solids, classifing particles into four groups and making a diagram shown in Figure 34. [55]

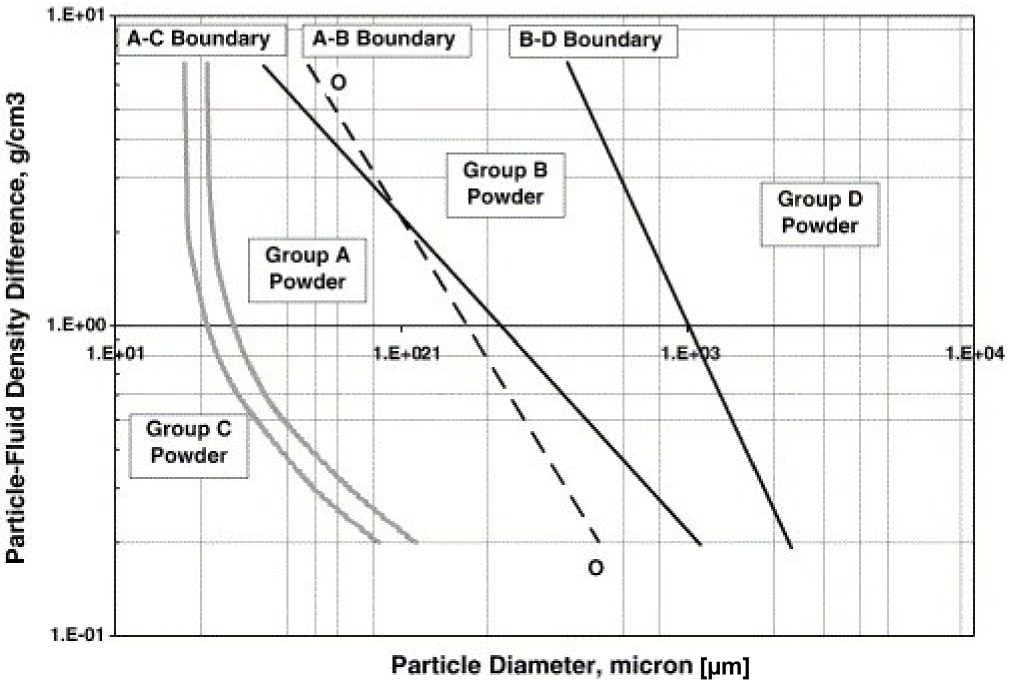


Figure 34: The original **Geldart's** classification of powders. [55]

Group A is designated as '**aeratable**' particles. The characteristic of these materials are a small mean particle size (dp< 30 µm) and/or a low particle density (<~1.400 kg/m^3). Group A powders expand homogeneously between the minimum fluidization velocity, and the minimum bubbling velocity (velocity at which the first bubbles appear). These solid particles allow an easy circulation around fluidized systems, cause a better circulation and mixing of solids and gas which leads to a high heat transfer coefficient. [54] [55]

Group B is called '**sandlike**' particles or bubbly particles. The approximate range of mean size of the materials in this group is within 40 to 500 µm, while the density is within 1400 to

4000 kg/m^3. Bubbles occur immediately after the minimum fluidization velocity has been reached and they can grow to a large size. Typically representatives of group B materials are glass beads (ballotini) and coarse sand (ordinary river or sea sand). [54] [56]

Group C materials are ‘**cohesive**’, fine powders which do not fluidize easily, because of the relatively large interparticle forces, compared to those resulting from the action of gas. They are prone to channeling in small diameter beds. Examples are talc, flour and starch. [54] [56]

Group D is called ‘**spoutable**’ and made of large or very dense particle. The fact that gas rises more quickly than bubbles causes gas to enter bubbles bottom and leave through the roof. If the gas distribution is uneven, spouting behavior and severe channeling can be expected. Roasting coffee beans and some roasting metal ores are examples of group D materials. [54] [56]

A very important feature for fluidized beds is **bulk density**, which is the mass of particles per unit of bed volume. Bulk density is always smaller than the true density of solids because it includes the voids of the fill. The parameters affecting bulk density are shape and size of the particles, particles surface and density and particle “packing” mode. The bulk density can be calculated from the following expression (Equation 1) [56]:

$$\rho_b = \frac{m_b}{V_b} = \rho_p(1-\varepsilon) \qquad \textbf{Equation 1}$$

If the used particles are very porous, it is necessary to include it in the equation. The void fraction of the bed is expressed with ε in the equation, whereby loose materials used with fluidized beds have 0.4 – 0.45 void fraction of the fixed bed. The bulk density of some materials is given in Table 10. [56]

Table 10: Bulk density of some particulate solids [56]

Material	ρ_b [kg/m^3]
Sand	1,200 – 1,400
Limestone	1,200 -1,400
Coal	600 - 800
Table salt	800 - 900
Cement	1,300 – 1,900

4.4.2 Gas-solid fluidization regimes

The two-phase system is an interaction of the solid particles and the fluid. It is a mechanical and hydrodynamic interaction but also an exchange of heat and mass as well as different chemical reactions occurring simultaneously. There exist a number of fluidization regimes as shown in Figure 35 [57]. When the gas starts to pass through the bed some of the particles can start to vibrate, but the bed height is not rising; this state is called a fixed bed. When the gas flow is getting higher, a point will be reached where drag forces of the gas equals the solids weight which leads to a bed growing. This point is called minimum fluidization and the gas velocity at this point minimum fluidization velocity. After that the formation of fluidization bubbles starts, the bubbling fluidized bed state is reached. With higher gas flow the bubbles are growing until they have nearly the same diameter as the bed; this is called slugging. If the gas flow rate is high enough, the velocity exceeds the terminal velocity of the particles and the upper surface of the bed disappears. Now, a turbulent motion of solid clusters and voids of gas of different sizes and shapes can be observed instead of the bubbles. At these conditions it is called a turbulent bed. With further increasing of the gas velocity, particles are starting to leave the reactor. At this point the pneumatic transport out of the reactor of the sand begins and there exist no more fluidized bed. [54] [57]

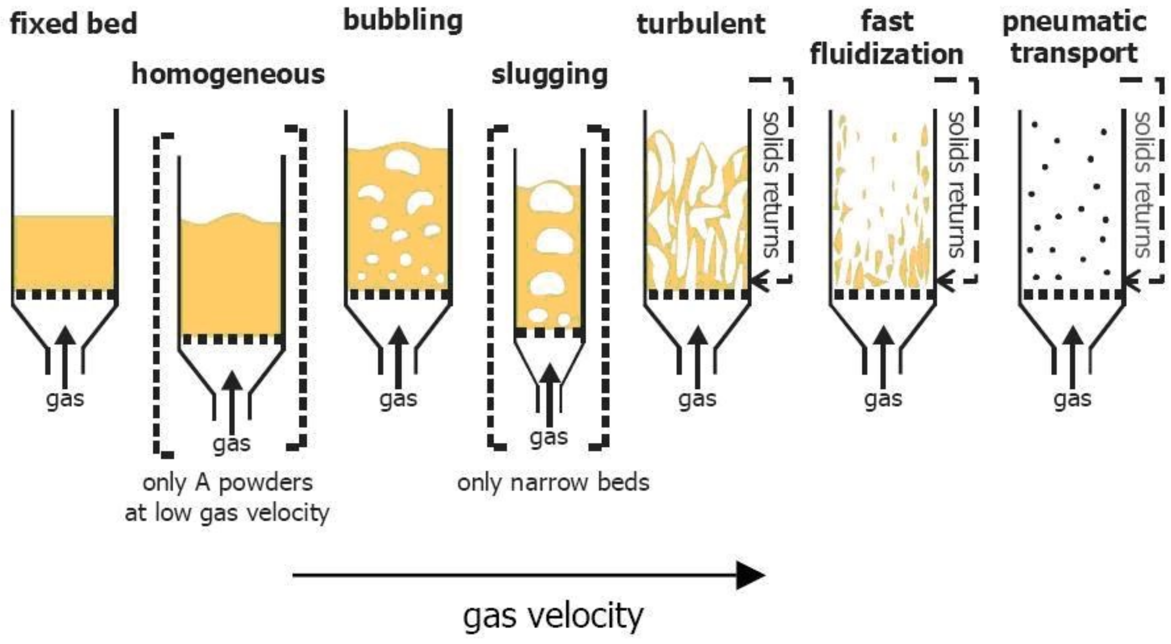


Figure 35: Gas-solid fluidization flow regime. [57]

4.4.3 Minimum fluidization velocity

The minimum fluidization velocity, U_{mf}, of a particulate solid is the velocity at which the particles start to float. The fluid pressure loss across the particles bed is equal to the apparent particles weight per unit area of the bed. The fluid pressure loos can be expressed like in Equation 2 where ρ_p is the density of the bed of particles fluidized by a fluid with the density ρ_f to form a bed of depth H and a voidage ε in a cross sectional area A. [58]

$$\Delta p = \frac{HA(1-\varepsilon)(\rho_p - \rho_f)g}{A}$$ **Equation 2**

Equation 2 can be simplified to Equation 3:

$$\Delta p = H(1-\varepsilon)(\rho_p - \rho_f)g$$ **Equation 3**

The simplest way to determine the minimum fluidization velocity is by using a diagram (Figure 36) of measured pressure drop as a function of velocity. The straight-line region OA in Figure 36 represents the packed bed region, where the particles are not relatively moving to one another. The range BC shows the fluidized bed zone. Before reaching the fluidized bed zone, at point A, the pressure loss rises above the predicted value given by Equation 2. The reasons for this value are the extra force required to overcome wall friction and the adhesive forces between bed and distributor. **U_{mf} is the minimum fluidization velocity at which the packed bed changes into a Fluidized Bed.** This velocity changes with the particle size and density and depends also on the fluid characteristics. [58]

U_{mf} has been studied since the beginning of fluidization research, and literature offers a wide range of correlations for minimum fluidization determination. However, theoretical prediction is difficult because of the many possible influences (design of the gas distributor, bed properties, vessel design, temperature changes, chemical reactions in the reactor, flow conditions, etc.). [58]

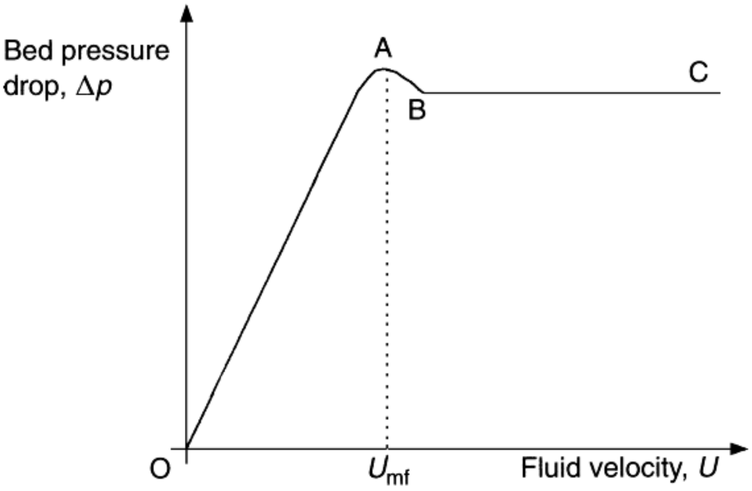


Figure 36: Pressure drop *versus* fluid velocity for packed and fluidized beds. [58]

4.4.4 Bed expansion and Fluidized Bed zones

Bed expansion in a fluidized bed can be explained as a decrease of bed density with an increase of flow rate. A simple way to describe the expansion is with a two-phase theory for fluidization, the bubbling phase (gas bubbles) and particulate phase (fluidized solids around the bubbles). Figure 37 shows the **two-phase model**, whereby Q is the gas flow rate and Q_{mf} is the gas flow rate when the fluidization starts. In this theory, it is assumed that any gas exceeding the required amount for the incipient fluidization will flow through the bed as bubbles. [56] [58]

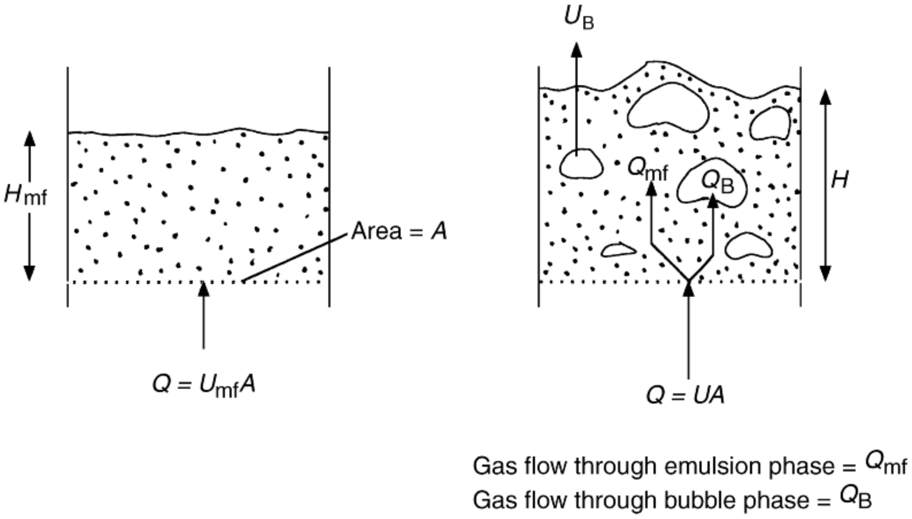


Figure 37: Gas flows according to two-phase model in fluidized beds. [56]

Q_B and Q_{mf} can be expressed with the following equations (Equation 4 and Equation 5) [58]:

$$Q_b = Q - Q_{mf} = \left(U - U_{mf}\right)A$$ **Equation 4**

$$Q_{mf} = U_{mf}A$$ **Equation 5**

Bed growing can be expressed in terms of fraction of the bed occupied by bubbles ε_B (Equation 6), where H is the bed height at U, H_{mf} is the bed height at U_{mf} and U_B is the mean rise velocity of a bubble in the bed. [58]

$$\varepsilon_B = \frac{H - H_{mf}}{H} = \frac{Q - Q_{mf}}{AU_B} = \frac{\left(U - U_{mf}\right)}{U_B}$$ **Equation 6**

Experiments have shown that this theory overestimates the volume of gas passing through the bed as bubbles. A better estimation can be made by replacing ($Q - Q_{mf}$) in **Equation 6** with Q_B (visible bubble flow rate) (**Equation 7**) [58]:

$$Q_B = \Upsilon A\left(U - U_{mf}\right)$$ **Equation 7**

The values for Υ are:

$0.80 < \Upsilon < 1.0$ for Group A powders

$0.60 < \Upsilon < 0.8$ for Group B powders

$0.25 < \Upsilon < 0.6$ for Group D powders

Entrainment rate and particle size distribution in a fluidized bed reactor will, in general, depend on particle size and density, gas properties, gas velocity, gas flow regime-radial-velocity profile and fluctuation as well as the reactor diameter. The reactor zones are shown in Figure 38 and described as follows [58]:

- Freeboard: Region between the bed surface and the gas outlet.
- Splash zone: Region just above the bed surface in which coarse particles fall back down.
- Disengagement zone: Region above the splash zone in which the upward flux and the concentration of fine suspended particles decreases with increasing height.
- Dilute-phase transport zone: Region above the disengagement zone in which all particles are carried upwards; particle flux and suspension concentration are constant with height.

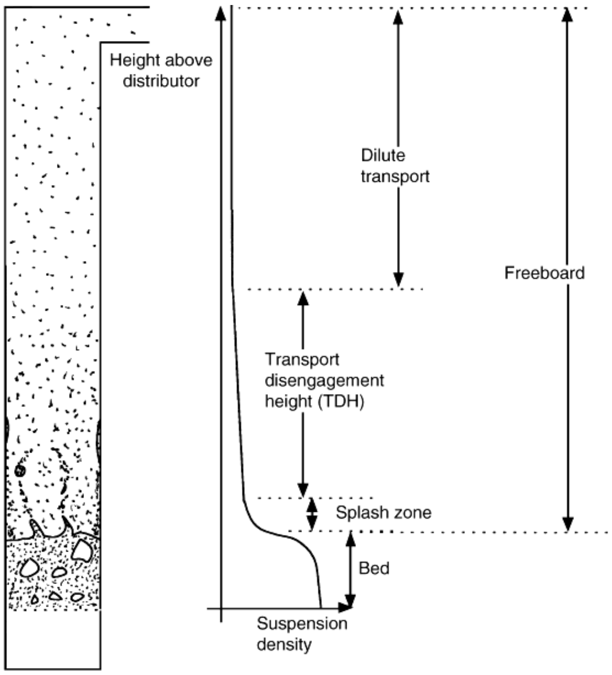


Figure 38: Zones in fluidized bed [58]

Theoretically, fine particles will be entrained in the flow and leave the reactor and coarse particles will stay in the system. Tests have shown that some fine particles may also stay in the system at several times their free fall (or terminal) velocity and coarse particles can also be ejected. The transport disengagement height (TDH) is defined as the height from the bed surface to the top of the disengagement zone. Above of this zone, the entrainment (ejection of particles from the surface of a bubbling bed) flux and the concentration of particles are constant. To get the maximum benefit from the effect of gravity in the freeboard zone, the gas exit should be placed above the TDH. [58]

4.4.5 Heat transfer in Fluidized Beds

The very good heat transfer is one of the advantages of Fluidized Bed reactors. The heat transfer occurs between solids, gas, reactor walls and internal surfaces of the equipment. In fluidized beds exist a uniform temperature distribution and the control is easy. There are two forms of heat transfer, gas-particle and bed-surface heat transfer. [56] [58]

The gas-particle coefficients for the heat transfer are small (5 – 20 Wm^2K). Since the particle surface area is very large, this form of heat transfer is rarely a limiting factor in reactors design and operation. Gas-particle heat transfer is an important factor in systems where a hot Fluidized Bed is fluidized by a cold gas. [58]

The bed-surface heat transfer coefficient in a fluidized bed between the bed and immersed surfaces (vertical walls or tubes) (Figure 39) may be considered to be made up of three components:

$$h = h_{pc} + h_{gc} + h_r \qquad \textbf{Equation 8}$$

Bed-surface heat transfer coefficient (h) in Equation 8 consists of the particle convective heat transfer coefficient (h_{pc}), gas convective heat transfer coefficient (h_{gc}) and radiant heat transfer coefficient (h_r). The heat transfer due to the motion of packets of solids that are carrying heat to and from the surface is described by h_{pc}. The heat transfer by the motion of the gas between the particles is given by h_{gc}. The solids are always circulating in the bed and transporting the heat continuously around the bed, whereby the limiting factor is the gas conductivity. [56] [58]

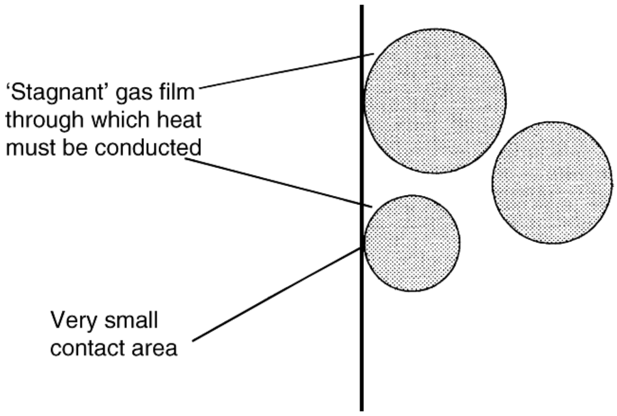


Figure 39: Heat transfer from bed particles to an immersed surface. [58]

It is also a fact that the solid particles have about thousands times the heat capacity of the gas on a volumetric basis. Also, the contact area between the particle and the surface is very small, which not allows a significant heat transfer. A lot of factors can affect the transfer, for example, a decreasing particle size reduces the mean gas film thickness and so improves h_{pc} (Figure 40). A higher gas temperature increases the gas conductivity and, as a result, improves h_{pc}. [56] [58]

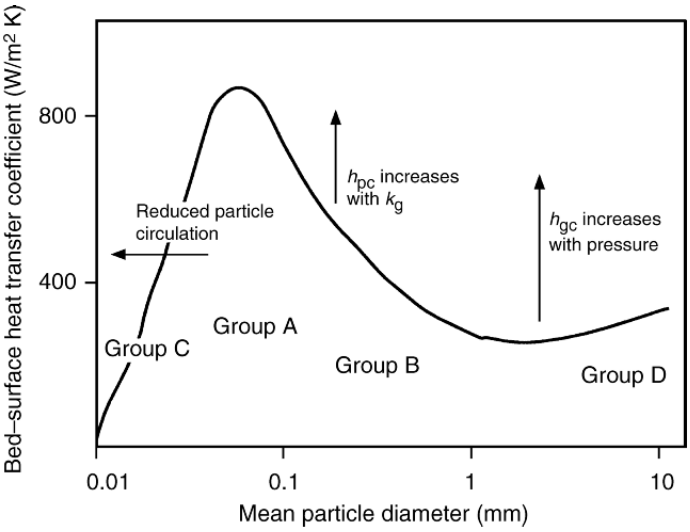


Figure 40: Range of bed-surface heat transfer coefficients with the different powder groups (see Figure 34). [56]

The gas velocity also has a big influence on the heating transfer, whereby with a higher fluidizing velocity the heat coefficient increases until a maximum h_{max}. After this point there is only a reduction because bubbles cover the surface for the heat exchange.

In the group of D powders (see Figure 34) the gas convective heat transfer is an important factor, because the solids fluidize at higher velocities. In this case, the gas specific heat capacity that rises with the pressure is important because the fluid transports the heat around in the bed.

When the process works with temperature over 600 °C, also radiative heat transfer is important and should be included in the calculations.

5 The PUCP bench scale pyrolysis plant

The bench scale pyrolysis reactor constructed during this PhD-work is based on the “**Hamburger Verfahren**” **(Hamburg method)**, which was developed in Germany at the University of Hamburg by a group of researchers leaded by Professor Hansjörg Sinn and Walter Kaminsky. They developed different sizes of reactors and bench scale plants. Fluidized Bed reactors working well based on the Hamburg method, have been proven in the field of pyrolysis and in different scales of applications. [59] [62]

The Hamburg method stands for a continuously operating fluidized bed pyrolysis. The fluidized material is stirred up from the bottom through a porous plate. Normally, silica sand is used as bed material. However, also catalytically active materials, such as zeolites (if they have adequate thermal stability and hardness) can be used. Nitrogen or pyrolysis gas (gas produced during pyrolysis and returned to the reactor after deposition of condensable products - loop operation) is used in this process for fluidization. The entry of oxygen is avoided to prevent combustion. Therefore, heating is done indirectly through burners or electric heaters. Such pyrolysis products are not mixed with combustion products.

The plant normally is supplied with two screw feeders. The first screw is used for metering and the second screw transports the material directly into the hot fluidized bed, where the decomposition takes place immediately (fast pyrolysis). After pyrolysis, the products are cooled and separated. [59] [60]

5.1 General description of the pyrolysis plant

A bench scale pyrolysis reactor was constructed at the Pontificia Universidad Católica del Perú (PUCP) to make first experiments with different feedstock. The plant is able to handle different turn of biomasses. Stainless steel was used as material for parts from the charging hopper to the cyclone. These parts are shown in a 3D graphic in Figure 41. The graphic also includes the support of the plant.

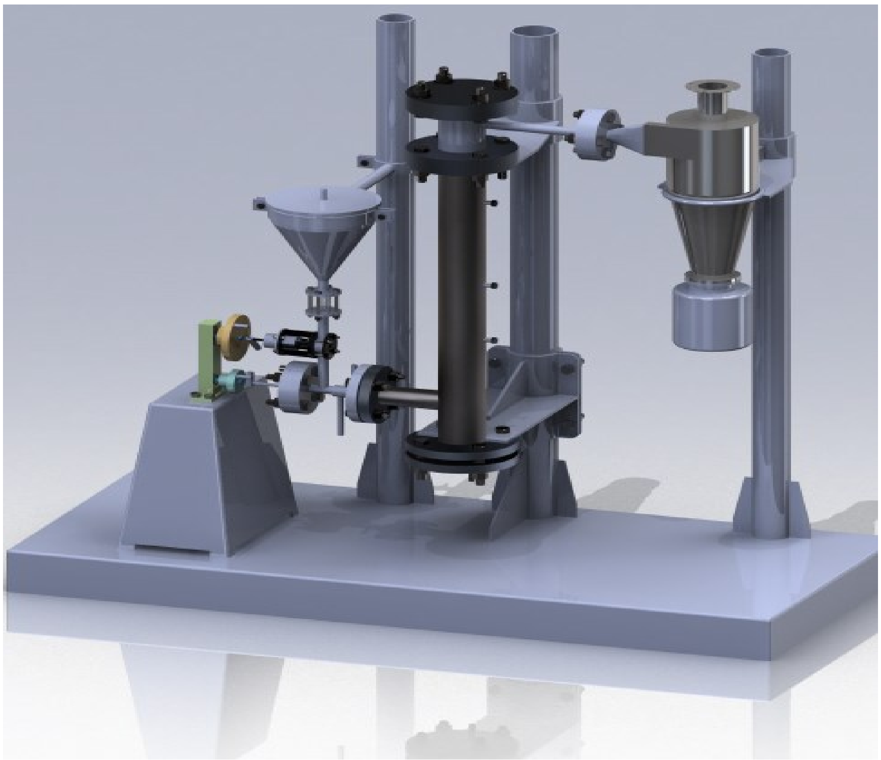


Figure 41: 3D graphic of steel parts of pyrolysis plant at PUCP.

The used steel is an austenitic Cr-Ni stainless steel with the number AISI 304. The components of this material are presented in Table 11. [63]

Table 11: Components of the AISI 304 steel [63]

DIN	X5CRNi1810	Ni [%]	8.0 – 10.5
AISI	304	Mn [max. %]	2.0
C [max. %]	0.07	Si [max. %]	1.0
Cr [%]	17.0 – 19.5	S [max. %]	0.03

This steel shows excellent resistance in alkaline solutions as well as organic and inorganic salts. In general, this material is highly resistant to corrosion (particularly in natural environmental media and in the absence of considerable chlorine and salt concentrations and sea water) and has reasonable weld ability. 304 Steel has good resistance to oxidation in intermittent service up to 870°C and in continuous service to 925°C. Applications with acids have to be checked individually. It is used in the crude oil industry, chemical industry, petrochemical industry, and automobile industry. [63] [64]

The construction work of the metal parts was carried out with Taller Elisa SRLtda. The other parts were constructed of borosilicate glass in the glass workshop of the University (PUCP).

Borosilicate glass (Pyrex®) is widely used for laboratory glassware. Borosilicate glass has excellent thermal properties with its low coefficient of expansion and high softening point. It also offers a high level of resistance to attack from water, acids, salt solutions, organic solvents and halogens. Resistance to alkaline solutions is moderate but strong alkaline solutions cause rapid corrosion of the glass. The chemical components of Pyrex® and some characteristics are shown in Table 12. [64]

Table 12: Chemical composition and some physical characteristics of Pyrex® glass (borosilicate glass). [64]

Physical Characteristics		**Chemical Composition**	
Linear Coefficient of Expansion [cm/cm/°C]	32.5×10^{-7}	SiO_2 [%]	80.6
Temperature limits [°C]	490 (extreme service) 230 (normal service)	B_2O_3 [%]	13.0
Softening point [°C]	821	Na_2O [%]	4.0
Density, annealed [g/cm^3]	2.53	Al_2O_3 [%]	2.9

The aim of the author of this PhD-work was to build the plant only with materials and parts available or produced in Peru. The challenges to accomplish research in a developing country are quite different compared to projects in Europe especially, the financial possibilities are very limited.

The flow chart of the pyrolysis plant constructed at PUCP in Peru is presented in

Figure 42. The process can be divided into three main stages:

1. Dosing and feeding of the raw material.

2. Transformation of organic mass in the reactor.

3. Collection and separation of the products.

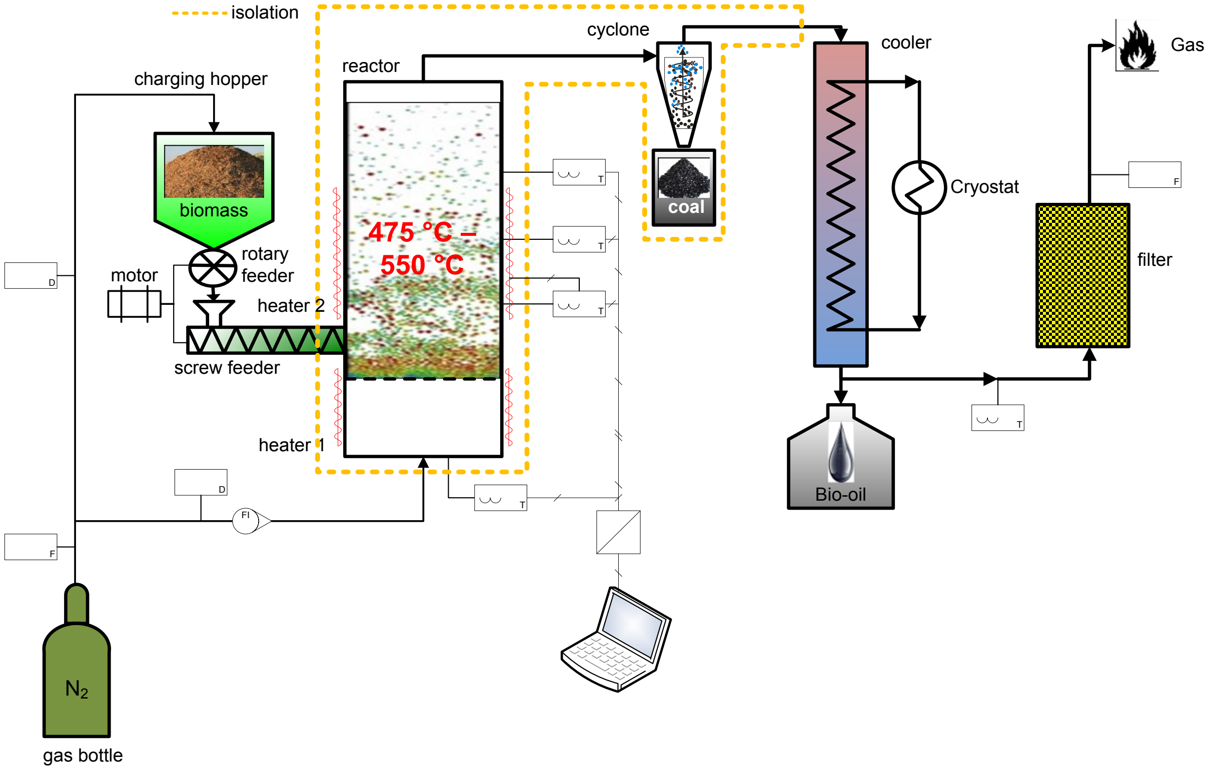


Figure 42: Flow chart of the pyrolysis plant at the PUCP

The raw material first is feed into the charging hopper and rinsed with N_2. The storage tank is connected with a rotary feeder that doses the amount of feedstock enter in the reactor by its rotations. A screw feeder, which follows after the rotary feeder, transports the biomass into the reactor. In the reactor, the chemical reactions occur to transform the biomass at temperatures between 475 °C and 550 °C. The reactor has an electric outside heating system and is isolated to minimize heat loss. The characteristics of the reactor are presented in Table 13. After the reactor, the separation and collection of the products begin. First, the gas comes to a cyclone where solid particles (char) are separated. The next step is the condensation of the oil in the cooler. The cooling liquid (a mix of water and ethylene glycol, 1:1) is cooled down to – 15 °C by a cryostat. The parts before the cooler are isolated, because the gas should come with the highest possible temperature to the cooler and then cool down very quickly. The last filter is only a control filter for removing all the particles which are left in the flow. In the end the gas is burned, for controlled disposal.

Table 13: Specifications of the PUCP reactor

Reactor type	Fluidized bed
Bed material	Quartz sand
Amount of quartz sand	50 – 200 g

Particle size of quartz sand	350 – 450 µm
Process temperature	450 – 600 °C
Process gas	Nitrogen (N_2)
Feeding	< 300 g/h
Particle size of feedstock	< 1 mm
Residence time in the reactor	0,5 – 2 s
Heating	Electric heating from outside
Thermocouple	Tipo K
Volume of the reactor	1.03 L

N_2 is used as fluidizing gas and to avoid the presence of oxygen in the system. The internal pressure used was a little bit higher than the ambient pressure. The system can be considered as a continuously operating reactor but it is limited by the amount of feedstock which enters the charging hopper. The reactor is built only to handle biomass. For experiments with other materials, for example plastics, another stainless steel would be necessary which also resist acids, because there is the possibility that acidic compounds may be formed in the reactor, like mentioned in publications. [59] [60]

5.2 Description of the individual components

5.2.1 Charging hopper

The charging hopper (Figure 43) is made of stainless steel and has a volume of 800 cm^3. Depending on the density, 0.5 kg to 1kg of feedstock can be stored in it. First experiments were made by using a mixer in the charging hopper to avoid bridging of the feedstock, but it did not make it better or worse, so it was removed. The cup of the charging hopper has an entry for the nitrogen to flush the system and push out the oxygen. To avoid the inflow of air ,an O-ring is put between the cup and the storage tank.

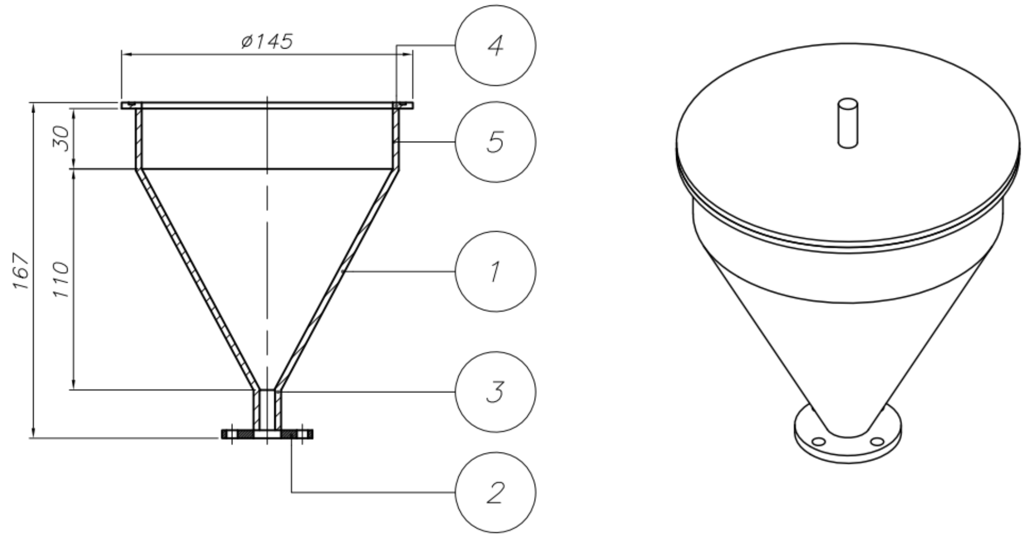


Figure 43: Charging hopper (the numbers in the circles are legends for the exact plans of the parts)

5.2.2 Rotary feeder

The rotary feeder (also called rotary valve) is the part of the installation, which doses the amount of biomass entering the reactor and consists of a rotor, a rotor case and a motor drive. The operation of the feeder is based on a rotor with certain number of blades, which turns in a closed fitting housing. [65] Material from the supply hopper continuously fills the rotor pockets (rotor case) at the inlet port (above the rotor). The motor-driven rotor then transfers it to the outlet where it is discharged into the conveying line. The result is a volumetric continuously conveying. The flow rate is determined by the contents of the rotor cell and the rotational speed of the rotor.[66] [67] A general design of a rotary feeder is shown in Figure 44. [67]

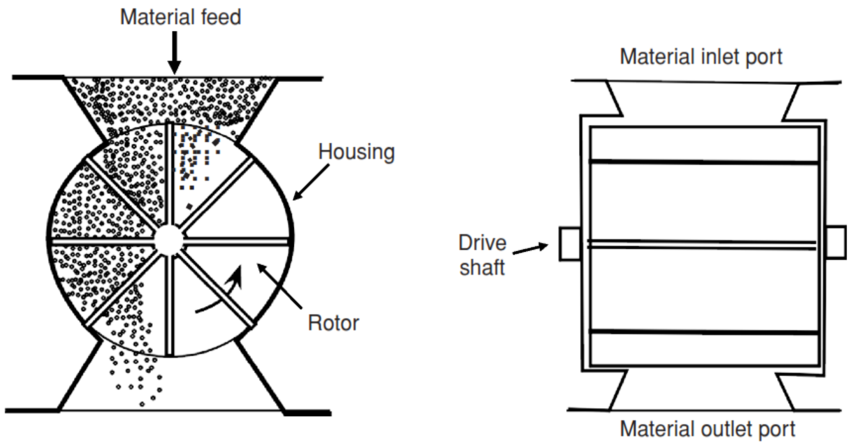


Figure 44: Drop-through rotary valve. [67]

The rotor cells have the forms of half cylinders, and a volume of 0.168 cm^3 (r = 0.4 cm, H = 1.3 cm) each. An experimental determination of the transport capacity for each feedstock has to be made because different feedstock have different bulk densities with various particle sizes, forms, etc. For example the rotary feeder transported 10.5 g semolina per 20 revolutions. A bulk density of 0.7885 g/cm^3 gives a volume of 0.6658 cm^3 per revolution. A comparison between experimentally determined and theoretically calculated volume of 0.673 cm^3 (4 rotor cells with a volume of 0.168 cm^3 each) shows, that they are nearly the same. Figure 45 shows the rotary feeder of the pyrolysis plant. The feeder and tubes are very small and therefore very dry feedstock can be used. If the material is wet, the danger of clogging is likely.

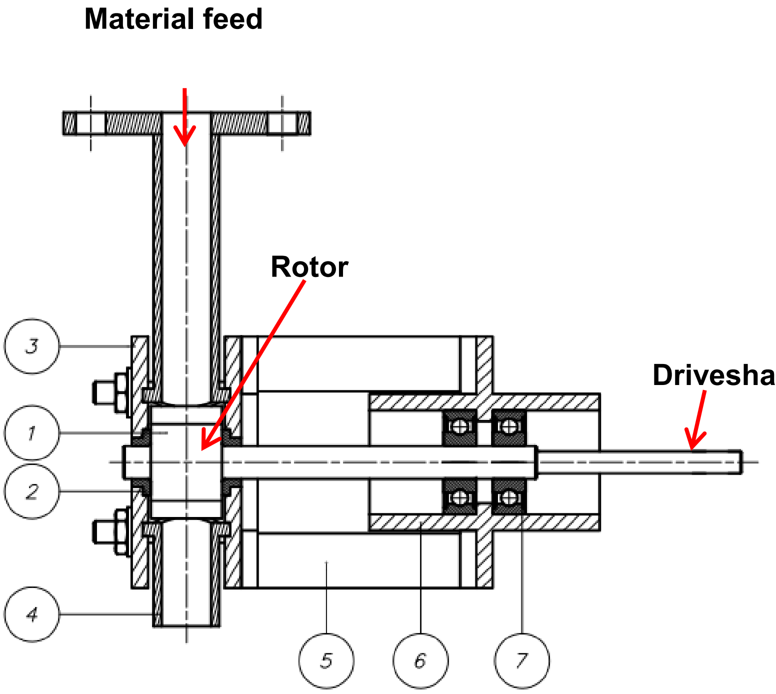


Figure 45: Rotary feeder (the numbers in the circles are legends for the exact plans of the parts)

The axis of the feeder is supported form two bearings, and connected to the motor over two discs.

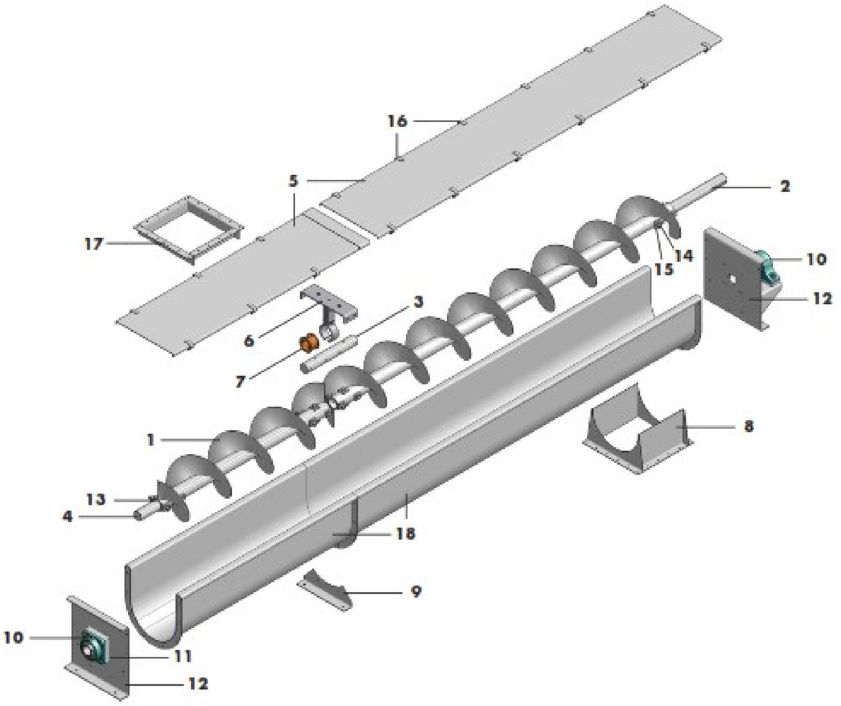
5.2.3 Screw feeder

The screw feeder or screw conveyor is one of the oldest methods of conveying materials. The original design is dating back to more than two thousand years in history. Over a century ago, screwdrivers came into a general use, for moving grains, fine coal and other bulk materials. Today, modern technologies have made the screw conveyor to one of the most efficient and economical methods to move bulk material. [68]

The main advantages of a screw feeder are [67]:

- An enclosed transport system, which protects the product and avoids contamination of the local environment (dust, vapors, gases, etc.).
- Only one working element, which does not need a return path.
- Screw conveyors can be equipped with jackets to serve as a drier or cooler too.
- They are compact, easily to adapt and have a great flexibility in capacity and transfer rate.
- Inlets and outlets of various sizes can be fitted.
- Reversible screws can be mounted on the same shaft to bring products to a central outlet, from two inlets.
- They can be used as a mixer or agitator to blend dry or fluid ingredients.
- They may be used for elevation and de-watering applications too.

One of the disadvantages of screw feeder is that lumpy, fibrous or sticky materials may cause problems. Another problem is the power requirements that can be high with solids that tend to packing. Lengths are limited by the allowable torque capability of the drive and coupling shafts. Efficiency decreases when the screws are inclined or vertically. The main parts of a screw conveyor are presented in Figure 46. [68] [69]



1) Screw; 2) Drive shaft; 3) Coupling shaft; 4) End shaft; 5) Covers; 6) Hanger; 7) Hanger bearing; 8) Discharge; 9) Flange foot; 10) End bearings; 11) Shaft seal; 12) End plates; 13) Internal Collars; 14) Coupling bolts; 15) Bold pads; 16) Cover clamps; 17) Inlet; 18) Troughs;

Figure 46: Components of a screw conveyor [68]

The “transport the bulk solids forwards”-mechanism is by material staying between two adjacent screw flights on the same axis promoted to slip down the face of the rising side of the flight when the screw rotates. The product is moved forward by this action at the rate of one pitch per rotation, assuming that the material does not spill over the center shaft and fall back into the proceeding pitch space. Figure 47 shows an enclosed screw conveyor identifying the different parts. [68] [69]

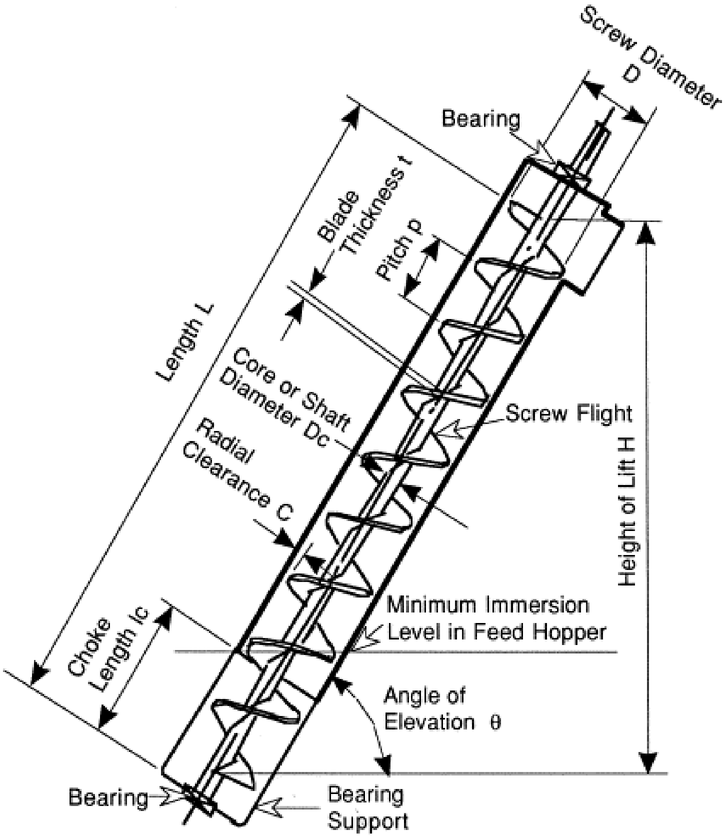


Figure 47: Description of an enclosed screw or auger conveyor. [68]

For the construction of the PUCP-pyrolysis plant, an approved screw conveyor is described in the literature [59]. This screw design was used because it worked very well in different experiments and the limited resources (personnel and financial) did not allow expensive equipment. It is a very small screw only for very fine particles up to 0.8 mm. The selected screw is pictured in Figure 48 and the characteristics are presented in Table 14.

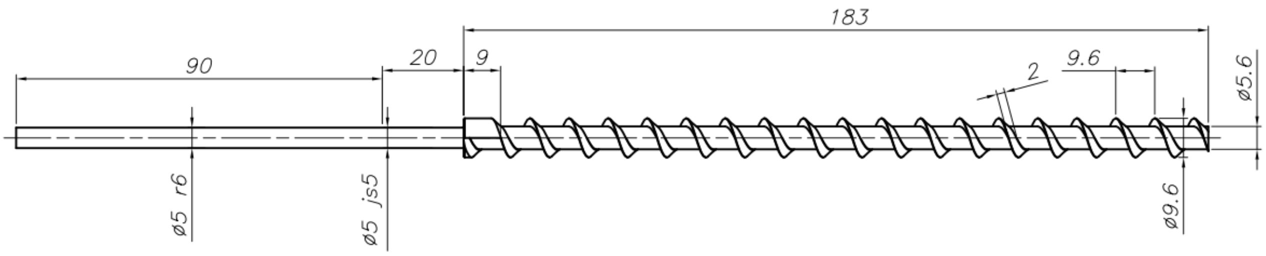


Figure 48: Selected screw of the PUCP-pyrolysis plant.

Table 14: Characteristics of the screw

Material	**AISI 304**
Screw length [mm]	183.0
Total length [mm]	293.0
Pitch [mm]	9.6
Screw diameter [mm]	9.6
Shaft diameter [mm]	5.6
Blade thickness [mm]	2.0

The screw is enclosed in a tube trough and has a jacket. The jacket can be used to cool the feedstock until it get into the reactor if it is necessary or it can be used to pre-heat the gas going in the rector. Cooling of the feedstock makes sense, when the material used changes its characteristics with higher temperatures. Also an early carbonization of the input material surface should be avoided, because it would encapsulate the particle with a thin layer of hard carbon. This layer makes the heat transfer and the reaction more difficult. [59] The whole system of the tube trough and the jacket is shown in Figure 49.

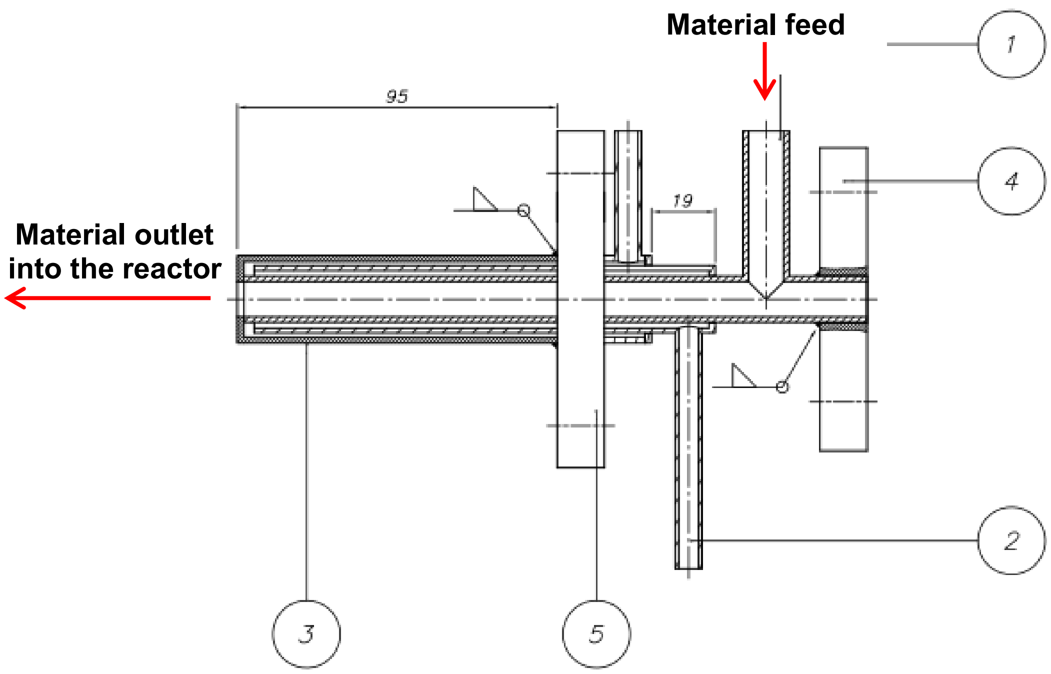


Figure 49: Construction details: the tube trough for the screw with its jacket (the numbers in the circles are legends for the exact plans of the parts).

The same motor powers the rotary feeder and the screw conveyor. The desired revolutions are controlled by a speed reducer (Figure 50). Experiments with semolina as input material showed that the rotary feeder has a capacity of 665.8 mm^3 per revolution in comparison to the screw conveyor with a capacity of 333 mm^3 per revolution. The screw conveyor has to spin at least twice faster than the feeder to transport the same amount of material. That is the reason why the two discs have a diameter of 803 mm and 415 mm respectively. The bigger one controls the rotary feeder and the smaller one the screw conveyor.

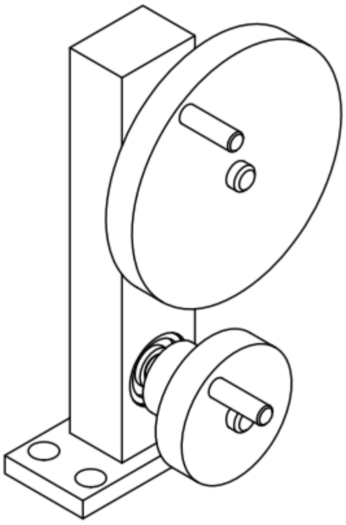


Figure 50: Speed reducer to control the rotary feeder and the screw conveyor.

Figure 51 shows a 3D graphic of the feeding system, including the jacket of the screw conveyor.

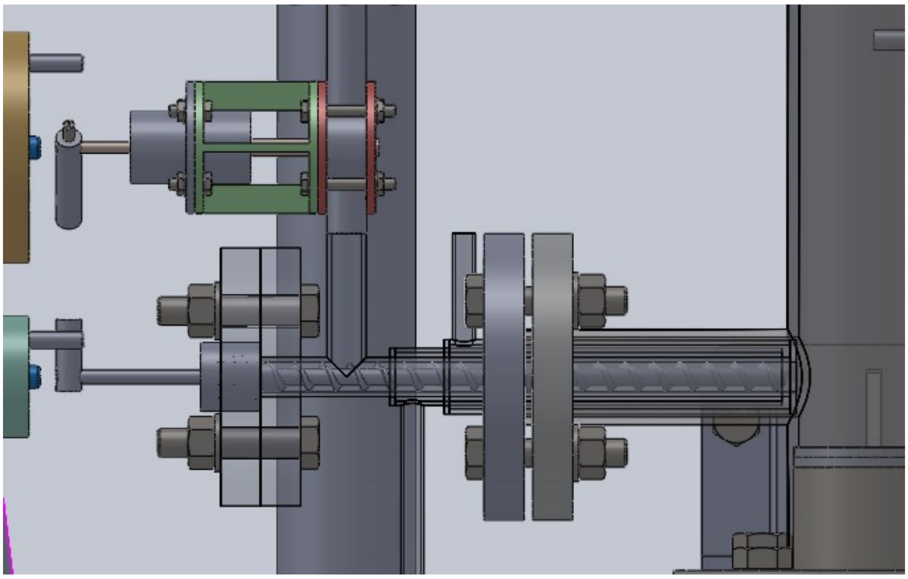


Figure 51: 3D graphic of the rotary feeder with the screw conveyor.

Some calculated transport capacities for different input materials are presented in Table 15. In fact, experiments have to be made with every material to get to know the exact transport capacity, because of the different size and behavior (form of the particles, force of attraction, agglutination, etc.) of different materials particles.

Table 15: Theoretical transport capacity for different materials

Material	Density [g/cm^3]	Theoretical transport capacity [g/rev]
Grounded coffee	0.41	0.137
Fine rice waste (grounded)	0.48	0.160
Coarse rice	0.72	0.240
Semolina	0.79	0.264

With all the moving parts, hermetic sealing of the conveyor is a major challenge. For the construction of the rotary and the screw feeders copper seals and special deep groove ball bearings (635–2RS1) with seals on both sides were used. The suffix 2RS after the type number indicates mounted sealing washers shields on both sides. These seals, made of rubber encased sheet steel reinforcement and finish on the inner ring with a sealing lip, have a high level of protection against dirt and moisture. The synthetic rubber is resistant to many aggressive substances.

5.2.4 Fluidized bed reactor with the gas distribution plate

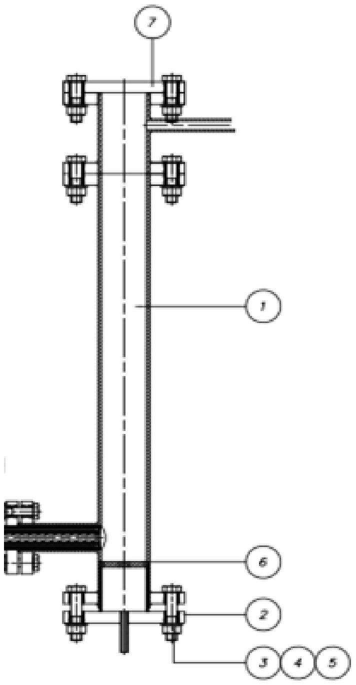


Figure 52: Reactor of the PUCP laboratory plant with the gas distribution plate

The reactor of the PUCP-pyrolysis plant (Figure 52) is 60 cm long and has an inner diameter of 52.3 cm and a wall thickness of 4 mm. The used steel is AISI 304. The upper part of the reactor with the gas outlet is made in a modular design, with the purpose that the reactor longitude as well as the design of the gas outlet can be changed for different experiments and approaches. Also, the gas distributor plate can be changed. For cleaning purposes, the lower and upper part of the reactor can be removed. In order to measure the inside reactor temperature, altogether 4 holes with small tubes are installed, in which 4 thermocouples can be fixed (Figure 52). The exact dimensions of the reactor and its devices can be seen in plans attached. The entry of the raw material occurs laterally into the fluidized bed. Quartz sand is used as bed material. The main pipe of the reactor is milled a few cm at the bottom to have a bigger inner diameter were the gas distribution plate enters. Over the plate, a very fine metal mesh was put to ensure that no solid particles are falling through the openings. The dimensions of the distribution plate (grid) are shown in Figure 54. A perforated plate was used, because it is simple to fabricate, it´s the most common solution, cheap, easy to modify hole size, easy to scale up or down and easy to clean. [70]

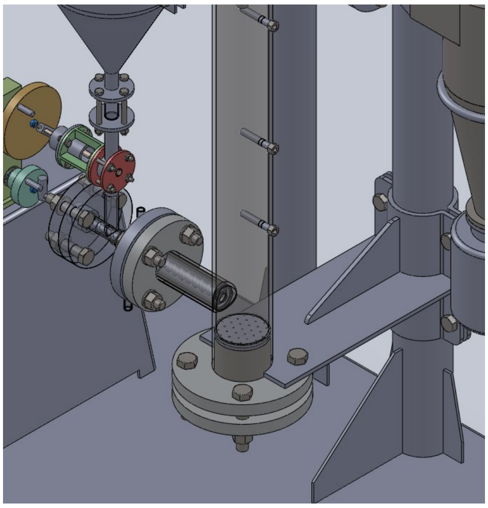


Figure 53: Lower part of the reactor with devices for the thermocouples and the gas distribution plate (grid)

For the design of the plate the following equations were used [70]:

$$\Delta P_{grid} = K g \rho_B L_B \qquad \Delta P_{grid} \geq 2.500\ Pa$$

Equation 9

$$V' = N \frac{\pi d_h^2}{4} U_h$$

Equation 10

$$U_h = C_d \sqrt{\frac{2\Delta P_{grid}}{\rho_{g,h}}}$$

Equation 11

$$L_h = \frac{1}{\sqrt{N_{d\ \sin 60}}}$$

Equation 12

For the Equations 9 – 12 the following nomenclature was used with:

C_d	Discharge coefficient
d_h	Grid hole diameter, [m]
g	Gravitational acceleration 9.8 m/s^2
K	Grid pressure-drop coefficient
L_B	Operating bed depth, [m]
L_h	Grid hole pitch, [cm]
N	Dumber of grid holes
N_d	Number of hole density (holes per unit area of the bed); [holes/m^2]
V´	Total volumetric gas flow entering the grid, [m^3/s]
U_h	Velocity of gas through the grid hole, [m/s]
ρ_B	Operating bed density, [kg/m^3]
$\rho_{g;h}$	Density of gas entering the grid hole (plenum conditions), [kg/m^3]
ΔP_{grid}	Pressure drop across the grid, [Pa]

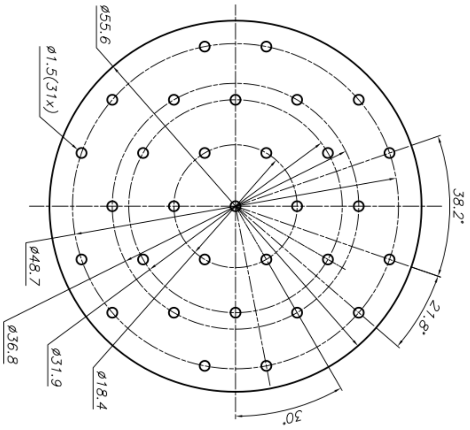


Figure 54: Dimensions of the used gas distribution plate

Gas flowing through the holes can develop different forms. There can be either a series of bubbles or a permanent jet; this depends on the operating conditions (e.g. pressure) and the system parameters. For the perforated plate design, the pressure drop across the grid is calculated with **Equation 9** where K = 0.3 for upward and lateral gas entry and 0.1 for downward gas entry. **Equation 11** is used to evaluate the gas velocity through the grid. A value of 0.8 is a typical value for the C_d. C_d depends mostly on the thickness of the plate and was calculated with the grid hole discharge coefficient design chart. To introduce the greatest number of small gas bubbles into the bed N should be maximized at the expense of d_h by using **Equation 10**. For the uniformity of fluidization it is common to lay out the holes in triangular or square pitch. In Figure 54 it is showed that triangular pitches were used to have more holes per unit area. L_h is the distance between the pitches and is calculated with **Equation 12** [70]. Copper seals were used between the different parts to make the reactor as hermetic as possible. Also, special stove putty, which resists temperatures up to 1,200 °C, were used to make the reactor gas proof. Both (the copper seal and the putty) have the advantage to resist high temperatures. The disadvantage of the putty is that it is not elastic and has to be changed from time to time.

5.2.5 Cyclone

Cyclones are plant components to separate a dispersed phase from a continuous phase. The difference in the mass density of the particles is used to separate the two phases by bringing them into rotation. The heavier particles are forced by centrifugal force to accelerate into the direction of the wall and moving downwards in the dust collector because of the gravity and the local flow. The cleared stream is than leaving the cyclone through the gas outlet. The principle parts of a cyclone are shown in Figure 55. [71] [72]

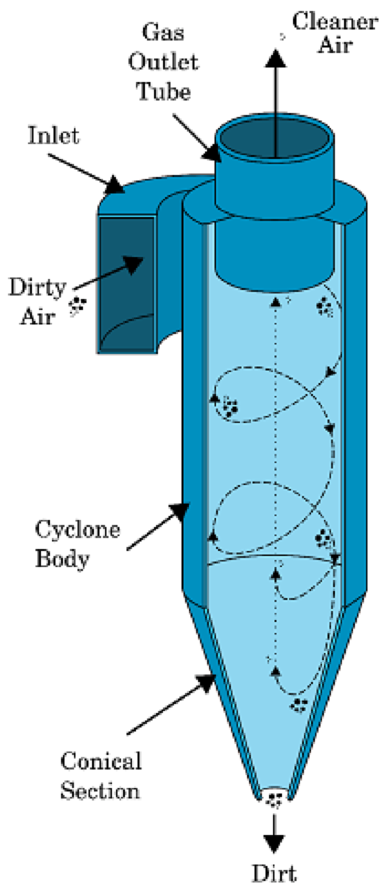


Figure 55: A typical cyclone separator. [71]

There are a lot of different forms and types of cyclones existing. In general, the advantages of this particle separation technology are [71]:

- Low capital cost
- No moving parts which means little maintenance and low operation costs
- Constant pressure drop
- Temperature and pressure limitations are only given by the used construction material
- Dry collection and disposal
- Small space requirements

The disadvantages of cyclones are [71]:

- Low output for low particle diameter (i.e.: not meant for fine dust separation),
- Unable to handle sticky or tacky materials,
- High efficiency units may experience high pressure drops.

There exist a wide variety of different possible factors and parameters that can influence the cyclone performance and flow pattern. These factors are [72]:

1. **Cyclone dimensions** (cyclone diameter, inlet height and width, dip tube diameter and length, cylinder height, cyclone total height, cone tip diameter),
2. Particle properties (density, shape, diameter and distribution, mass loading),
3. Gas properties (velocity, density, viscosity, temperature, pressure,
4. Other factors (wall roughness, shape of dip tube and eccentricity of vortex finder).

For the construction of a cyclone several inlet configurations can be applied, as can be seen in Figure 56 [72].

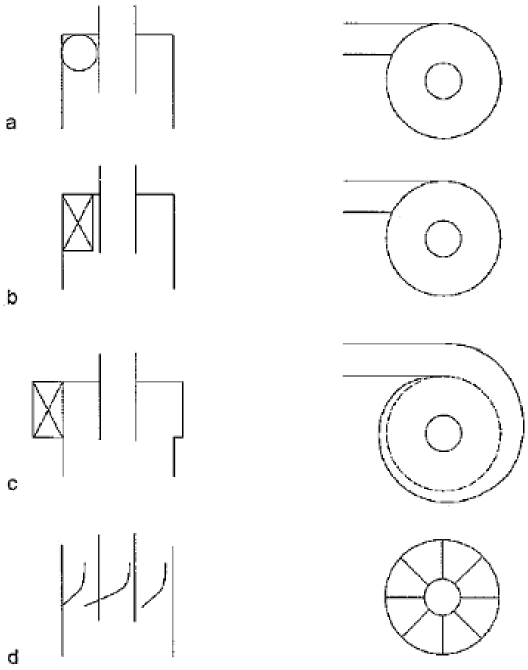


Figure 56: The four most used inlet configurations; on the left = side view; on the right = top view: (a) circular or 'pipe' inlet; (b) 'slotted' (also called 'rectangular' or 'tangential' inlet) inlet; (c) 'wrap-around' inlet and (d) axial inlet with swirl vanes. [72]

a) The simplest type is a **circular pipe**. This type of inlet does not need a round-to-rectangular transition section. It is a cheap solutions for applications in which some sacrifice in separation performance is acceptable, like in several woodshop and grain processing units.

b) This **tangential inlet** normally is used in chemical and petroleum processing industries. The inlet is placed at the same radius as the cyclone barrel. A ring of circulating dust can appear along the inner roofline but fortunately this ring does not affect the cyclone performance.

c) In this **"wrap-around inlet"** type of cyclone, the area for flow is decreased which means that the gas flow undergoes some acceleration upstream. A wrap-around inlet produces a larger momentum compared to a slotted (tangential) inlet with the same cyclone diameter. The reason is that the inlet is positioned at a larger radius than the cyclone barrel.

d) In this **axial inlet** case, the flow enters parallel to the cyclone axis. This type is more often inserted in cylindrical-bodied cyclones rather than in cylinder-on-cone or conical-bodied geometries. One advantage of the axial inlet is the high axial symmetry in the flow.

For the **PUCP-pyrolysis plant, tangential inlet** (configuration b) was chosen. The dimensions for the cyclone were calculated with the following equations [73]:

$$\Delta p_i = 0.9 \times \Delta p_{total}$$ **Equation 13**

$$\Delta \rho_i = \xi_i (\rho_L/2) v_i^2$$ **Equation 14**

$$r_i = \sqrt{\frac{V'}{\pi v_i}}$$ **Equation 15**

For the **Equations 13 – 15** and for the calculation with the characteristic factors the following nomenclature was used with:

Δp_i	Pressure drop in the dip tube [Pa]
Δp_{total}	Total pressure drop [Pa]
ξ_i	Pressure drop coefficient
V'	Volumetric flow rate [m^3/h]
r_i	Diameter of the dip tube [m]
v_i	Average dip tube velocity [m/s]
ρ_L	Gas density [kg/m^3]
u_i	Gas tangential velocity at r_i [m/s]
r_a	Outside radius cyclone [m]
h_i	Height of separation space [m]
h_{total}	Height of the cyclone [m]
b	Width of inlet [m]
h_z	Length of body [m]

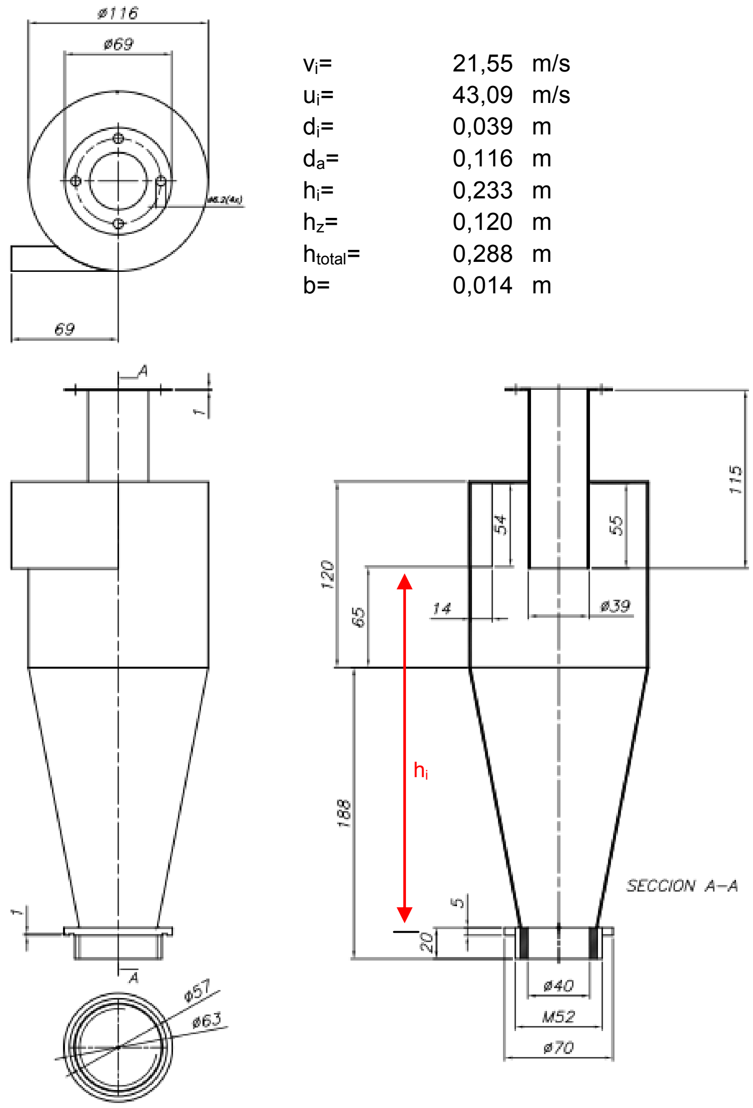
The pressure loss in the dip tube (Δp_i) was approximately calculated with **Equation 13**. With the **Equation 14** the velocity in the dip tube (v_i) was calculated. In the next step, the (r_i) was calculated (**Equation 15**). The other dimensions were determined by using the characteristic proportions for a cyclone with a tangential inlet and the assumptions are presented in Table 16. [73]

Table 16: Assumptions and characteristic specifications for a cyclone with tangential inlet

Assumption for the cyclone used	
Volumetric flow rate; V'	1.5 m^3 / h
Loading; μ_e	< 0.1
Density (solid); ρ_{solid}	1,100 – 2,600 kg/m^3
Density (gas) N_2 at 500 °C; ρ_{N2}	0.517 kg/m^3
Pressure drop; Δp_{total}	2,000 Pa

Pressure drop in the dip tube; Δp_i	1,800 Pa
Pressure drop coefficient; ξ_i	15
Characteristic factors (for a tangential inlet)	
u_i/v_i	2
r_a/r_i	3
h_i/r_a	4
Δp_i	$0.9*\Delta p_{total}$
h_{total}	$h_i + h_i*0.25$
b/r_a	0,25
h_z/r_i	6.666

With **Equation 14** - **Equation 15** and the data presented Table 16, the dimensions of the cyclone depicted in Figure 57 were calculated. It hast to be mentioned that the thread at the bottom of the cyclone to connect the char collecting bin is not included in the calculated dimensions of the cyclone.



v_i= 21,55 m/s
u_i= 43,09 m/s
d_i= 0,039 m
d_a= 0,116 m
h_i= 0,233 m
h_z= 0,120 m
h_{total}= 0,288 m
b= 0,014 m

Figure 57: Dimensions of the cyclone constructed for the PUCP-pyrolysis plant.

5.2.6 Cooler

After the gas passed the cyclone and the solid particles are separated, it is cooled down in a helically coiled heat exchanger (cooler), where also the liquid parts are condensed. At the bottom of the condenser the oil is collected. The heat transfer rates in helical coils are higher as compared to those in straight tubes. Due to the compact structure and high heat transfer coefficient, helical coil heat exchangers find extensive use in industrial applications such as power generation, nuclear industry, process plants, heat recovery systems, refrigeration, food industry, etc. [74]

The used condenser is a coil condenser made out of glass. Figure 58 shows the basic structure and operation of a coil condenser. The gases enter with high temperatures the condenser (countercurrent operation mode) and are cooled down very rapidly. The cooling liquid (ethylene glycol-water mixture) was cooled down before with a cryostat (Messgeräte - WerkLauda, JL TRA Kryostat UK 30 L) to a temperature of - 15 ° C. The oil is condensing on the walls and is running down into the glass were it is collected. The gases are leaving the condenser and are passing through two more traps that are cooled down with ice water. For the calculation and design of the condenser, which were made in the glass laboratory of the chemical department of PUCP, the following assumptions were made:

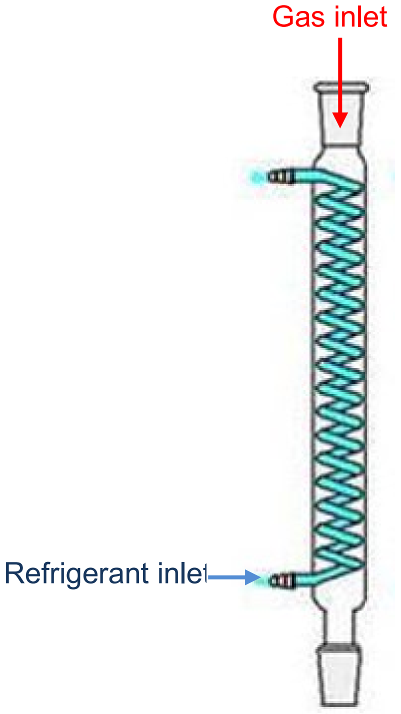


Figure 58: Coil condenser used in the project

- Constant gas flow and pressure.
- The volumetric flow changes with temperature.
- The internal diameter is used for the calculations.
- Temperature difference gas: ΔT_{gas}= 430 °C
- Temperature difference refrigerant: ΔT_{ref} = 5 °C
- Turbulent flow with an average value.
- All the used values are for N_2, because the main part of the gas will be N_2 and the other parts of the gas are not exactly known.

The calculations shown below have been used for the determination of rough design data of the heat exchanger. For more accurate calculations the material properties and the flow rate of the media are crucial and have to be considered too. Also during different experiments the flow properties, the flow rate and other parameters will change. For the condenser design calculation the following equations were used (**Equation 16 - Equation 19**) [73]:

$$Q = \frac{V' c_p \rho \Delta t}{3600}$$ **Equation 16**

$$A = \frac{Q}{k\Delta T_m}$$ **Equation 17**

$$\Delta T_m = \frac{\Delta T_{gr} - \Delta T_{kl}}{ln\frac{\Delta T_{gr}}{\Delta T_{kl}}}$$ **Equation 18**

$$k = \frac{1}{\frac{1}{\alpha_1} + \frac{d}{\lambda} + \frac{1}{\alpha_2}}$$ **Equation 19**

For the **Equations 16 – 19** the following nomenclature was used with:

Q	Amount of heat [W]
V´	Volume flow rate [m^3/s]
c_p	Specific heat capacity [kJ/kg K]
Δt	Tempreture difference [K]
ΔT_m	Log mean temperature difference [K]
ΔT_{gr}	Temperature difference between the two streams at the entry [K]
ΔT_{kl}	Temperature difference between the two streams at the outlet [K]
ρ	Density gas [kg/m^3]
k	Thermal transmittance [W/(m2*K)]
α_1	Heat transfer coefficient cooling liquid [W(m^2*K)]
α_2	Heat transfer coefficient gas [W(m^2*K)]
λ	Heat conductivity [W/(m*K)

With **Equation 16** the required quantity of heat (Q) to cool a medium is calculated. In this case Q is the quantity of heat, which has to be removed from the refrigerant. The heat exchange surface (A) is the necessary surface for the cooling process as calculated with **Equation 17**. **Equation 18** gives the mean logarithmic temperature difference. **Equation 19** is used to determine the thermal transmittance (k). The used condenser has an inner tube with a longitude of 1.2 m and an inner diameter of 0.005 m. The theoretic heat quantity for the first experiments is 0.4 kW per hour. It is assumed that the amount of heat to be dissipated and absorbed is equal. Radiation heat losses are neglected. [73]

Table 17: Values for the calculation of the condenser

Used values for the design calculation	
Density N_2; ρ_{N2}	0.8 kg/m^3
Specific heat capacity N_2 (at 450 °C); $c_{p,N2}$	1.104 kJ/kg K
Volume flow rate; $V´_{gas}$	3.5 m^3/h

Heat exchange surface; A	0.002 m^2
Temperature difference gas; ΔT_{gas}	430
Temperature difference refrigerant; ΔT_{ref}	5
Heat transfer coefficient H_2O; $\alpha_{1,H2O}$ (turbulent flow)	2,000 $W/(m^2*K)$
Heat transfer coefficient gas; $\alpha_{2,gas}$ (turbulent flow)	50 $W/(m^2*K)$
Heat conductivity glass; λ_{glass}	0.93 $W/(m*K)$

These calculations were made to control if the used condenser with an exchange area of 0.01884 m^2 is able to cool down the gases. The calculations showed that the exchange area theoretically should be enough (the area is a lot of times larger than the calculated minimum area) to cool down the gases.

After the condenser two other cooling traps to collect the oil were installed. These traps are working with ice water and were only safety provisions for the case that not all of the oil was condensed before.

5.2.7 Filter

A mineral wool filter (Figure 59) was the last trap before the gas was burned for disposal. This is a control filter with the purpose of separating all the solid and liquid particles not collected in the traps. After this last cleaning step the gas was burned and then emitted into the fume cupboard of the laboratory. In this first phase of the project the gas was not analyzed or collected.

Figure 59: Control filter of the pyrolysis plant: new installed filter (on the left); filter after the experiment (on the right)

5.2.8 Heating system

Figure 60: Radiant process heaters (Stock CRB E-Mitters) used in the project

To heat the reactor, three solid, curved face ceramic E-Mitters (Stock CRB E-Mitters, color – metamorphing Rose to Grey) were used (Figure 60). Each one of the heaters has 1,000 W with a Watt density of 6.69 W/cm^2. The heater body can reach temperatures up to 771 °C. The body of the heater also includes a thermocouple type K. These E-Mitters have 3-1/2" ceramic bead insulated leads. The dimensions of the heaters used are shown in Figure 61. [75]

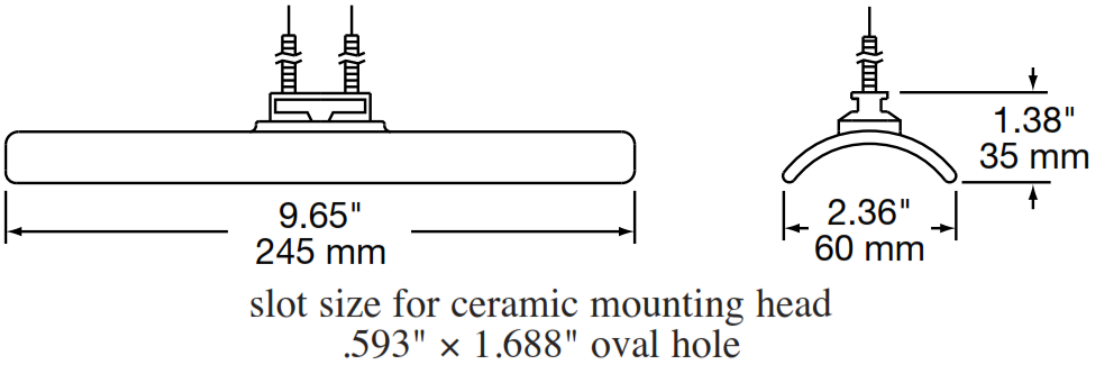


Figure 61: Dimensions of the heater (Series CRB) used in the project

For the preheating of the PUCP-pyrolysis plant also 3 heating jackets (50 W each) were installed. These heating jackets help to heat up the systems.

5.2.9 Other parts

The PUCP laboratory plant also includes a gas bottle for the fluidization gas. The instruments of the gas bottles are regulating the pressure and the gas flow rate. Starting from the reactor up to the cyclone, all the parts are isolated with mineral wool. This should avoid the loss of heat and also is a protection for the persons working with the equipment, because temperatures can reach nearly 600 °C. The system includes altogether 6 different thermocouples to control the process. One thermocouple is connected with the heaters to control the temperature in the reactor. A temperature controller turns the heaters on and off to hold the desired temperature in the reactor.

The PUCP-pyrolysis plant is fixed to a frame (Figure 62). The frame was constructed with a minimum of fix points as possible, to take care of the thermal extension of the material. The Calculations for the thermal extension showed that the elongation of material should not be more than 1 cm and so it does not have that much influence. The frame consists of a base plate and three stands with holding devices for the different parts of the equipment. The frame is made out of the same stainless steel like the other parts. The holding devices are for the storage tank, the reactor and the cyclone.

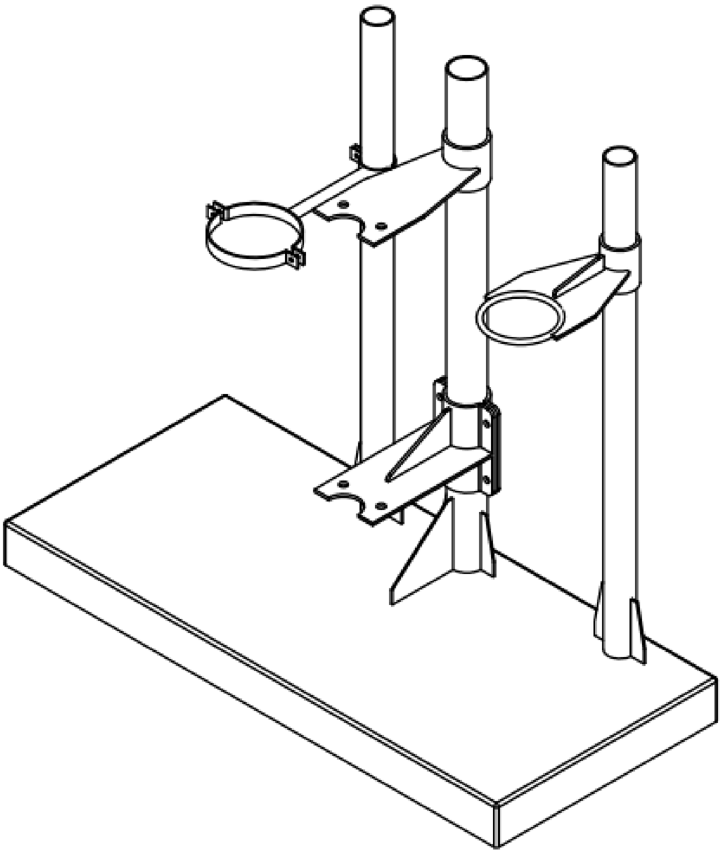


Figure 62: Frame for the PUCP-pyrolysis plant

After the fabrication of all the different parts described in this work the plant was assembled for the first time, which is shown in picture Figure 63. The picture shows the plant without gas and electric installations; also the heating system and the isolation are missing.

Figure 63: Assembled PUCP-pyrolysis plant without heating, electric installations and isolation.

6 Experiments

As reported in chapter 5, after design and construction of several components, the PUCP-pyrolysis plant was assembled and electricity and gas lines were installed. After the completion of the reactor, and the choice of starting material, the first experiments were carried out. These first fundamental tests were used to make the final adjustments of the plant. At the same time, also different possible input - raw materials for the first experiments were tested.

6.1 Assembling and installation of the pilot plant

During the reactor assembly, different aspects must be considered. First, the different parts have to be connected in such a way that no gases from inside can escape and no oxygen from outside can enter. The other important point are the high temperatures during the experiments. Therefore, only high temperature resistant materials can be used for connecting. One critical part is the connection of the metal tube from the cyclone with the glass condenser, where a graphite gasket was used to seal the crossover and also to protect the glass.

Different flanges (DIN 2527 and DIN 2573) were applied to connect the different tubes and parts. In Figure 64 the installation of heaters and thermocouples can be seen.

Figure 64: Installation of the heaters and the electric system in the PUCP-pyrolysis plant

As mentioned before, three heating elements were attached to the reactor tube and connected with the controller (THOLZ MDH). The total system is equipped with its own electrical circuit and circuit breaker.

In Figure 65, the control valves for the gas installations are shown. These devices control the pressure and the flow (L/min) of the nitrogen which is used for the fluidization and to generate an oxygen-free atmosphere.

Figure 65: Control valves for the nitrogen flow and pressure adjustment

The self-constructed PUCP-pyrolysis plant with the isolation is shown in Figure 66. As shown in the picture, the hot parts of the reactor are isolated with mineral wool and covered with aluminum foil. On the right site, two flexible and isolated tubes are connected to the condenser. These tubes are coming from the cryostat to cool down the gases which are entering into the condenser. Under the condenser, there is one glass vessel followed by two other traps to collect the oil. During the experiments, these glass vessels are immersed in an ice-water bath. After these traps the gases are leaving the tube and are burned after passing the last control filter. The system is also equipped with an interface to store the temperature data on a computer. Due to electrical noise this interface was not working very well and needs to be improved in the future. To measure the temperature on the different surfaces, an infrared thermometer (UNI-T; UT302C) was used.

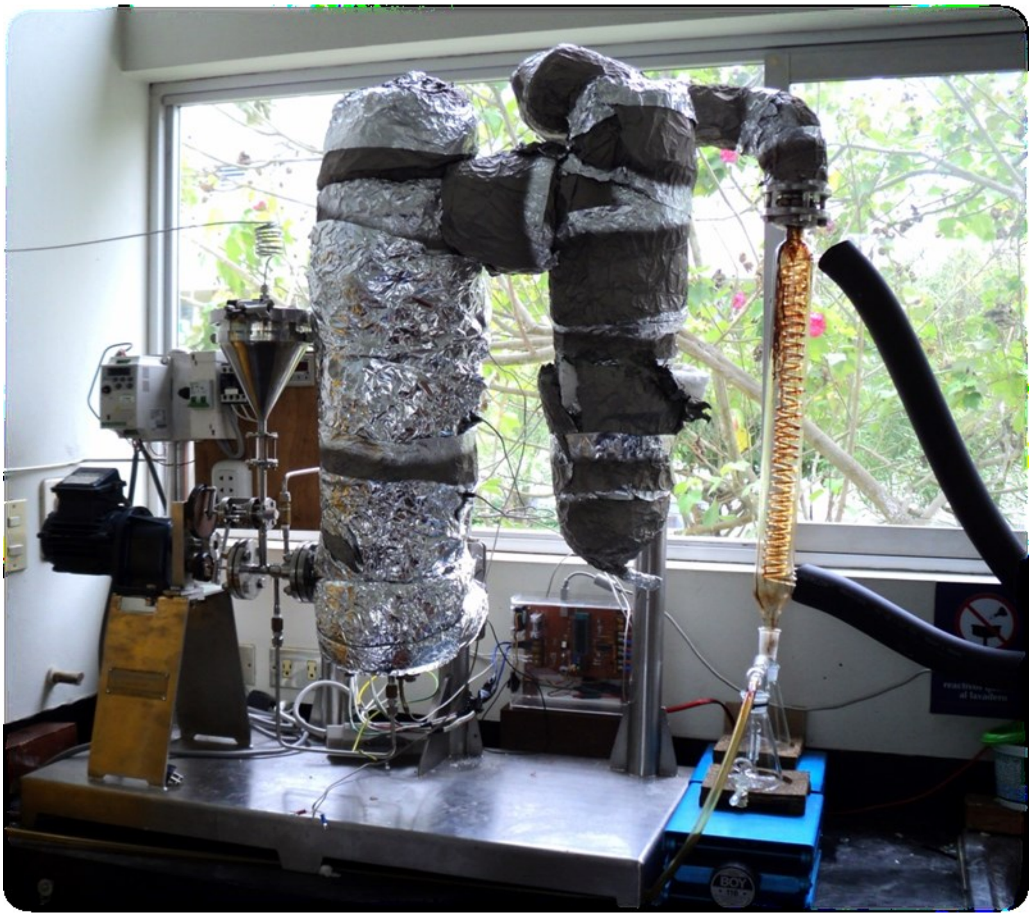


Figure 66: Constructed plant showing isolation and condenser.

6.2 Operating Test of the reactor

6.2.1 Testing the heating system

After completion of the construction and installation phase, the reactor was tested. First, the reactor was gradually heated up slowly to bring the reactor to a maximum temperature of 650 °C. It proved that the heaters reached the desired temperature fast and that they worked very well. It was also proven that the materials used withstand the high temperatures without major problems.

6.2.2 Leak test

Another important investigation concerns the leak test. For this purpose, the corresponding parts of the plant were covered with soapy water and checked for bubbles. If a small leak was identified, it was sealed and the test was repeated until no more bubbles were formed. Because of the moving parts 100% tightness is not possible, but with the leak test the losses could be reduced to an acceptable minimum. In order to prevent the penetration of oxygen, the working pressure during the experiments was set to 1.2 bar (overpressure), which means in case of leaks that no oxygen would penetrate from the outside but the process gases are pushed outwards.

6.2.3 Testing the raw material input

Also the raw material input into the reactor was tested. This test has to be made for any type of raw material separately, as different densities, particle sizes and forms need different speeds of the motor. The biomass storage tank has a nitrogen entry to avoid oxygen entering in the reactor. At last, the cooling liquid temperature in the cryostat was controlled.

6.3 Raw materials used

Different types of raw materials were considered for the pyrolysis experiments. One goal was to find suitable materials which can be collected at the PUCP campus and that are also available all over Peru. Some basic experiments were made to identify the most suitable input raw material. The selected bio-waste materials were: cooked chicken bones, grass, raw potato shell, banana peel, cooked rice and coffee grounds.

The different organic waste materials were placed in an oven to determine water content and dry mass. With a bomb calorimeter Cusson P6310 (Figure 67) the calorific value (HHV) of the samples was determined according to ASTM standard D240 - 02. The percentage of inorganic mass was calculated from the unburned rests which remained in the test capsule. The results obtained are shown in Table 18.

Figure 67: Bomb calorimeter in the PUCP laboratory

Table 18: Calorific value (HHV), inorganic and dry mass for different matrices

	Calorific value (HHV) [kJ/g] DM	Dry mass [%] OS	Inorganic mass [%] DM
Coffee grounds	19.10	52.74	1.11
Banana peel	17.09	9.20	9.48
Potato shell	15.88	13.75	5.99
Cooked chicken bones	15.48	44.22	35.44
Grass	15.28	27.98	10.61
Cooked rice	15.21	34.87	0.74

Results indicated that **coffee grounds** and **cooked rice** were the most suitable materials for the first group of experiments. Both have a low percentage of inorganic material, which means less solid residues would remain and obstruct the reactor. Also, the percentage of dry mass for both materials is relative high. A higher percentage of dry mass means less energy needed to dry the biomass, in other words, a better energy balance.

6.3.1 Used coffee grounds

For the first experiments, coffee grounds were chosen because of homogeneity and easiness of availability both at PUCP and elsewhere. The preparation of this coffee waste for the experiments is not very labor-intensive. The coffee grounds sample was collected in the Coffee house “338” (Figure 68), a very popular coffees shop where students and professors use to go. Over there, they use a different Arabic coffee beans mixture produced in Peru for the preparation of their favorite coffee.

Figure 68: Picture of the coffee shop where the coffee grounds sample for the experiments was collected.

In households or coffee shops raw coffee powder is contacted with hot water or steam under conditions favoring the release of aroma compounds and other coffee-bean constituents into the liquid. From these operations, a solid residue, the coffee grounds, are generated as waste. In general, the amount of coffee grounds is steadily increasing in line with the growth of coffee consumption all over the world. [76]

Peru is not only exporting special kinds of coffee all over the world but also the consumption within the country is rising. In general, coffee is the most widely traded tropical agricultural commodity in the world, mainly used for beverages, with a production of 145 million bags (*i.e.* 4,200,000 in Peru) in 2013 (one bag weighs 60 kilograms), whereby Brazil is the biggest producer of coffee beans. Depending on coffee varieties, the amount of oil that can be recovered varies from 11 to 20 wt% [77]. With the increase of coffee production and consumption, the volume of coffee grounds is also growing. In Peru, normally, coffee grounds are put into the household waste that goes mainly to landfills. In some cases, this waste is used as compost or deodorizer, but large amounts are unused and can be converted into renewable energy [76].

Also, the food and beverage industry is generating the by-product coffee grounds (from the extraction process during the treatment of coffee powder and instant coffee preparation) which can be readily utilized for energy generation either on-site or in centralized utilities.

The advantage of processing the waste “**coffee grounds”** at a nearby location, where the coffee waste is generated, is to reduce or eliminate the requirement for collection and transportation which would save energy and costs. Another time and energy consuming process to prepare the coffee waste for the pyrolysis is **drying**. The industrial waste is known as “soluble coffee ground” and is classified as “Class II Waste – non inert” according to NBR 10004 (Brazilian Standard for the classification of solid wastes). Mostly, this waste is used as a substitute fuel for co-incineration in utility boilers. [78]

The coffee grounds composition and characteristics can vary, depending on the different coffee beans and preparation processes. In Table 19, some more general average data of dried coffee grounds is presented. [77]

Table 19: Some characteristic data of dried coffee grounds [77]

	Coffee grounds
Water content (wt%)	1.31
Volatile (wt%)	77.51
Fixed carbon (wt%)	19.83
Ash (wt%)	1.35
Elements (wt%) (dry, ash-free basis):	
C	54.61
H	6.59
O	34.83
N	3.97
S	0
HHV* (MJ/kg)$_{DM}$	22.74
LHV* (MJ/kg)$_{DM}$	21.22

*HHV = Higher Heating Value; LHV = Lower Heating Value.

6.3.2 Preparation of the raw material for the experiments

As reported before, the coffee grounds were collected from the Coffee house “338”. After collection, the raw material was dried in an oven at 105 °C for 24 hours, and the coffee waste was sieved to get a homogeneously material with particles between 0.1 and 0.5 mm. The dried and sieved coffee grounds were stored in transparent glass bottles in a glass desiccator for future use.

For the described pyrolysis experiments a dry and homogeneous raw material is important, to ensure a trouble-free entry of biomass in the reactor by avoiding bridging and clogging. An input raw material with low water content is also important for the quality of the pyrolysis oil recovered, because the water would be in the liquid product of the process.

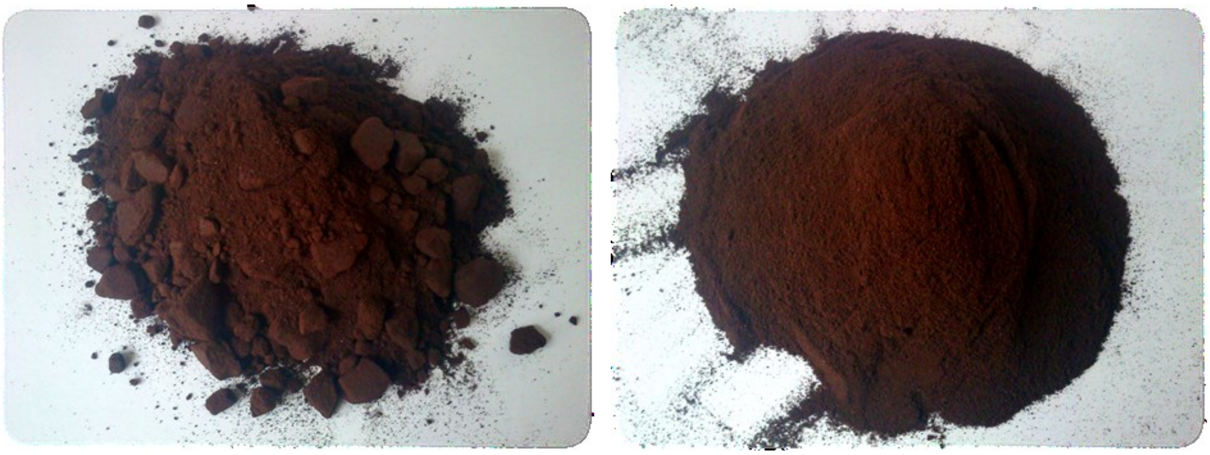


Figure 69: Coffee grounds after collection (left picture) and dried and sieved (right picture)

6.4 Tests performance

The established PUCP-pyrolysis reactor type has a fluidized bed characterized by good temperature distribution and favorable mass and heat transfer properties. For these experiments, biomass particles with < 1 mm were used and heated very quickly (within seconds) to the final temperature in the reactor. SiO_2 (quartz sand) particles were the bed material of the reactor. The organic feedstock particles are disintegrated to char, gases, tar and water vapor. N_2 is used as fluidization gas and also dilutes immediately the gases and vapors produced in the reactor and transports them out into the cyclone. The solid output particles (char) are separated in the hot cyclone before the gas flows into the condenser were condensation of tar, oil and reaction water takes place.

The first experiments with the described biomass (i.e. coffee grounds) were made to test the equipment and look for possible improvements because no previous data or practical experience was available. All the experiments were carried out three times under the same conditions with the general parameters listed in Table 20. The presented results are mean-values (if not otherwise stated). First tests with different temperatures were made to determine the optimum temperature at which the highest oil yield can be achieved. After these series of experiments, the effect of different fluidization gas streams has been studied. For all these tests, coffee grounds were used as raw material.

Table 20: General operating conditions for the pyrolysis experiments

Throughput	300 g/h
Used raw material (coffee grounds) per experiment	250 g
Particle size of biomass	0.1 – 0.5 mm
Amount of quartz sand (bed material)	100 g
Particle size of quartz sand	0.3 – 0.45 mm
Temperature cryostat	-15 °C
N_2 – flow for inertisation/fluidization	2 L/min
Average residence time	1 - 2 sec

The experimental procedure at the **PUCP-laboratory flash pyrolysis plant** can be divided into following phases:

- Weighing and assembling,
- Heating,
- Pyrolysis and products recovering,
- Cooling,
- Disassembling and weighing,
- Cleaning process.

Weighing and assembling

The following parts and materials have to be weighed before and after the experiment (Table 21):

Table 21: Parts and materials which are weighed before and after the experiment

Before:	**After:**
• Amount of biomass. • Amount of quartz sand. • Charcoal collecting bin (empty). • Cooler (after cleaning process).	• Quartz sand with remained char particles in the reactor (after 3 single experiments). • Charcoal collecting bin (full). • Cooler (after 3 single experiments).

• Cooling Traps. • Filters (after 3 single experiments). • Connection tubes.	• Cooling Traps. • Filters (after 3 single experiments). • Connection tubes.

Not all single parts are weighed after each single experiment, because the dissembling process is very laborious and the sealing of the reactor could suffer. In addition, the oil deposits in the not always weighted parts are very low and in the range of measuring errors. In this case, the parts are weighed after 3 trials (each experiment is repeated 3 times with the exact same parameters and conditions) only and the results adapted accordingly.

The assembly begins with the insertion of the metal mesh at the reactor bottom. In the next step the reactor is filled with quartz sand and closed at the top. During all steps it is necessary to ensure that the sealing rings are in the right place and position and that the screws are tightened enough to ensure tightness. Following the feedstock storage, the container is closed after charging the biomass into it. Screwing of the biochar collecting bin and the installation of the condenser are the following steps. The other cooling traps are placed in a container which later is filled with ice/water-mixture. The last steps are the connection of all the parts after the condenser with tubes and also with the cryostat. It should be mentioned that the long tube between the cyclone and the condenser has to compensate the temperature-induced reactor expansion. For that reason, the attachment of the condenser remains vertically displaceable. The connection of the metal tube with the glass condenser can be crucial, that is the reason why the construction has to be made in such a way to compensate expansions and reduce tension between parts (especially when they are made of different materials). In the next step, the removable isolation is put again over the parts which will be heated up. After the nitrogen pipelines are connected, the plant is ready to be used.

Heating

It is important that the system heating can be done at different temperature intervals, which means that when the heaters are switched on, the value of the temperature control is set to 100 °C. When this temperature is reached, the control is set to 250 °C, then to 400 °C, and finally to the desired end temperature. The reason is, this avoids system overheating and the process is safer. Together with the heaters, also the screw conveyer and the gas flow (N_2) are switched on. After the first experiments, also other heating elements were installed (3 heating jackets) helping to heat up the system. When the system reaches the necessary temperature for the experiment, this state is maintained for 15 min to stabilize the system until the entry of biomass in the reactor starts. During the trial, temperature fluctuates due to the heating control system inertia and the biomass entry, that is the reason why this increased value is necessary to hold a desired test temperature + / - 15 degrees.

Also the cryostat is switched on to cool the cooling liquid for the condenser.

Pyrolysis and products recovering

Shortly before the start of the biomass entry, all temperatures and flows are controlled. It must also be ensured that all tubes are properly connected. During the process, the relevant parameters must be carefully controlled. A drop in the fluidized bed temperature of about 10 °C at the beginning and also small fluctuations during the experiment will lead to the selection of higher temperature values for the temperature control.

It is also important to check, if the biomass feedstock is leaving the charging hopper because bridge formation in the storage tank could appear and interrupt the biomass stream. In case the biomass stream has already stopped by knocking or beating the biomass tank gently, the bridge formation can be eliminated.

The deposition of liquid on the condenser must be observed too. If the condensate covers a large part of the glass surface, the condenser can be heated slightly with a hair dryer so that the condensate (oil) flows into the reservoir. The oil reservoir also has a discharge cock which can be used to empty it.

In general, all the flows and the gas burning have to be controlled, because it may happen that it comes to blockages because of different reasons in different parts of the plant. After the whole biomass feedstock has entered the reactor, the gas flow into the condenser has to be observed closely. When the product gas stream in the cooler is noticeably weaker the motor for the screw conveyer can be turned off and the gas flow can be throttled. The gas flow helps to cool down the plant and also to avoid unwanted combustion reaction.

Cooling

When the temperature in the reactor becomes less than 300 °C, the gas flow can be turned off. To speed up the cooling, all the removable parts of the isolation (i.e. reactor dome, isolation of char collecting bin, etc.) are removed. To shorten the dripping time of the oil the condenser can be heated slightly with a hair dryer as mentioned before. After the whole oil has been collected, the equipment can be disassembled and the different parts can be weighed. As the PUCP-pyrolysis plant is working in the high temperature range, safety gloves have always to be used. It also may happen that the hot quartz sand escapes from the reactor so safety glasses are a must for the operating personal.

Disassembling and weighing

Disassembly, in the case that it has not yet done, is performed in reverse sequence to assembling. This is followed by reweighing of the different parts mentioned in Table 21.

Cleaning process

For cleaning of the parts made out of glass, all adhering products are removed and collected as good as possible (mechanically or by gentle application heat) from the individual system components. After the first cleaning step, the glass pieces are put in aqueous sodium hydroxide (10 %) solution. At the end, the parts are cleaned with distilled water and dried before reused in the next experiment.

The metal parts (i.e. reactor and cyclone) are manually cleaned to remove the deposits on the surface walls. If it is necessary, also sodium hydroxide can be used to get off the incrustations. It is very important to collect the removed crust and scale as good as possible, because they are needed for the material balance and calculation of the gas production. In the first experiments, the gas production of the process was calculated by the simple approach: **solid products + liquid products + gas = 100 %**.

The parts in front of the reactor (i.e. storage tank, rotary and screw feeder) are cleaned with a brush and compressed air. At the end, the entire equipment can be cleaned with compressed air too.

6.4.1 Data collection

The data obtained during the tests are recorded in a protocol. Mass measurements are performed before and after the experiment. During the experiments, temperature pressure and material flows need to be checked, observed and documented.

Mass determinations: All gravimetric measurements of solid and liquid feedstock as well as products, and the system parts were carried out with a laboratory balance, OHAUS Adventure Pro AV8101, which reading accuracy is 0.1 g. There was also a Miray Bmr-53 balance available, with a reading accuracy of 1 g for coarser measurements.

Temperatures: The temperature data of the heating, the fluidized bed and the connecting tube are measured by thermocouples type K, displayed by a temperature controller 3-digit digital display with 0.1 °C (Tholz MDH). There was also an IR Thermometer (UNI-T UT302C) available to measure the temperature at different parts of the PUCP-pyrolysis plant.

Pressures: Pressure values are not directly included in the protocol, but can be continuously read from gauges. A commercially available pressure reducer on the nitrogen gas bottle shows the reservoir pressure (0-300 bar) of the bottle and the outlet pressure by pressure reduction to (0-15 bar). The nitrogen gas bottle is in a storage area outside the laboratory. This gas bottle is shared with other laboratories. A precision pressure regulator (0 - 16 bar, Linde) regulates the pressure for the pyrolysis plant. There are two flow meters installed after the pressure regulator to control the gas flow (0 – 25 L/min and 0 – 10 L/min respectively)

Biomass feedstock flow: The entry is controlled by a rotary valve connected to a motor (Figure 70). A Delta VFD-L AC motor drive (Figure 70) regulates the revolutions per minute and so the biomass feedstock flow rate. For each feedstock, how much biomass enters per revolution has to be tested first because this value differs, depending on particle, particle size, density, etc.

Figure 70: Specifications of the motor for the rotary valve and the motor drive regulator Delta CFD-L

6.5 Fundamental experiments

The first experiments were performed with 60 g coffee grounds and a gas flow of 12 L/min. These experiments brought an oil yield of about 35 – 38 wt%. In these experiments, enlarged deposits at the pipes wall surface after the reactor and the cyclone could be observed. These deposits were a mixture of viscous oil and char and lead to clogging of the tubes (Figure 71). To solve this problem, **three additional heating elements** (heating jackets with 50 W each) were installed and the holding time after reaching the desired temperature in the reactor and the beginning of the experiment was increased. The new heating jackets were installed around the cyclone and two at the tube, connecting the cyclone with the condenser. These alterations were made to heat up the tubes and the system faster and prevent premature condensation.

Figure 71: Deposits in the tubes during the first experiments.

6.5.1 Effects of different temperatures

After the modifications of the PUCP-pyrolysis plant, experiments with 3 different temperatures (i.e. 475 °C, 500 °C, and 525 °C) were carried out to determine at which temperature the highest pyrolysis oil yield can be obtained. The temperature is one of the most important parameters in a pyrolysis process. Each experiment was repeated three times under same conditions. For these test series, 60 g coffee grounds as feedstock and 12 – 13 L/min N_2 for the fluidization of the bed were used. All other parameters are shown in Table 20 and the results are presented in Table 22.

Table 22: Influence of different temperatures on the product yields of pyrolysis process

	Experiment A		**Experiment B**		**Experiment C**		**Average Value per 100 g biomass**		
Temperature	Oil [g]	Cokel [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Gas* [g]
475 °C	22.1	12.1	24.8	11.5	24.9	14.1	**39.8**	**21.0**	**39.2**
500 °C	25.4	11.8	28.3	12.8	27.4	12.5	**45.0**	**20.7**	**34.3**
525 °C	20.5	9.7	23.4	10.4	24.5	10.7	**38.0**	**17.2**	**44.8**

*calculated values (100 % - % oil - % char = % gas)

6.5.2 Effects of different gas flows

In these experiments, the effects of three different gas flow rates (i.e. 10 L/min, 12.5 L/min, 15 L/min) on the product yields were evaluated. Each experiment was repeated three times with exact the same parameters: 60 g coffee grounds and pyrolysis temperature of 500 °C. All other unchanged parameters are shown in Table 20 and the results are presented in Table 23.

Table 23: Influence of different gas flow rates [L/min] on the product yields of pyrolysis process

	Experiment A		**Experiment B**		**Experiment C**		**Average Value per 100 g biomass**		
Gas flow	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Gas* [g]
10 L/min	22.4	10.5	25.0	11.0	25.8	11.1	**40.7**	**18.2**	**41.1**
12.5 L/min	22.9	11.3	25.2	11.5	26.7	12.8	**41.5**	**19.8**	**38.7**
15 L/min	23.0	11.8	26.9	12.7	26.4	12.3	**42.3**	**20.5**	**37.2**

*calculated values (100 % - % oil - % char = % gas)

6.5.3 Experiments with higher amounts of biomass feedstock

In the first sets of experiments, only 60 g coffee grounds was used for the experiments. In this test series higher amounts of raw material input were used to see how it affects the oil yields. As a conclusion from the previous tests, 500 °C and a gas flow of 15 L/min were chosen as optimum parameters for these experiments. All the other unchanged parameters are shown in Table 20 and the results are presented in Table 24.

Table 24: Influence of different amounts of biomass feedstock on the product yields

	Experiment A		**Experiment B**		**Experiment C**		**Average Value per 100 g biomass**		
Amount of biomass feedstock	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Oil [g]	Coke [g]	Gas* [g]
200 g	81	56	86	58	80	45	**41.2**	**26.5**	**32.3**
300 g	118	54	142	60	123	63	**42.6**	**19.7**	**37.7**

400 g	189	64	192	72	193	68	**47.8**	**17.0**	**35.2**

*calculated values (100 % - % oil - % char = % gas)

6.6 Products

6.6.1 Pyrolysis oil

Around 90 % of the oil formed in the pyrolysis process is collected in a modified Kitasato flask under the condenser. This flask has a discharge cock to empty out the oil (Figure 72). The pyrolysis gas is leaving the flask through a tube and goes to the other traps where the rest of the oil is collected. Small amounts of the liquid product also stick at the walls in the connection tubes. To collect the total amount of oil as good as possible, all the concerned parts of the equipment are warmed gently and the liquid is collected in a flask (normally in a modified Kitasato flask).

Figure 72: Erlenmeyer flask to collect the oil of the pyrolysis process (on the left) and the pyrolysis oil (on the right sight)

Regarding the main product, the collected oil separates in two phases. The lighter phase is a dark liquid much more viscous than the heavier one. To separate the two different liquids, the oil was separated in a pear shaped separating funnel (Figure 73). The two separated phases are shown in Figure 74.

Figure 73: Pear shaped separating funnel for phase-separation of pyrolysis oil

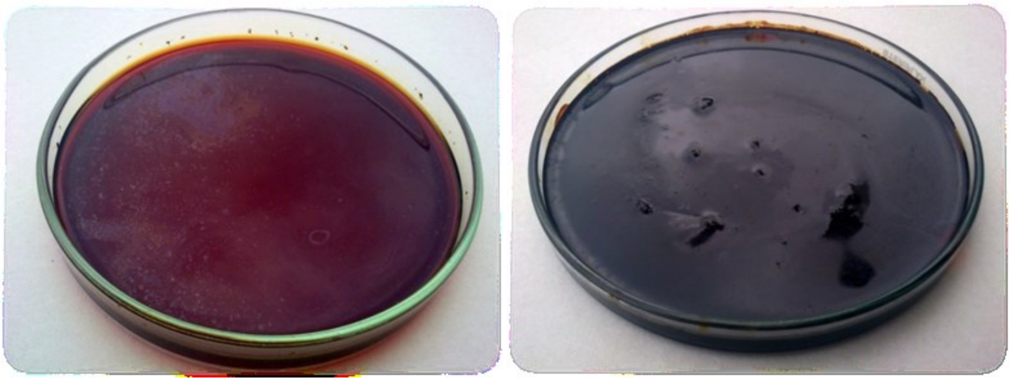


Figure 74: The two different phases of pyrolysis oil after separation

One interesting thing is the effect of temperatures on the viscosity and homogeneity of the two different phases. At room temperature, both liquids are quite uniform and can be easily and thoroughly mixed. If the temperature is lowered, the properties of the lighter liquid change, and it becomes thicker. This effect is shown in Figure 75.

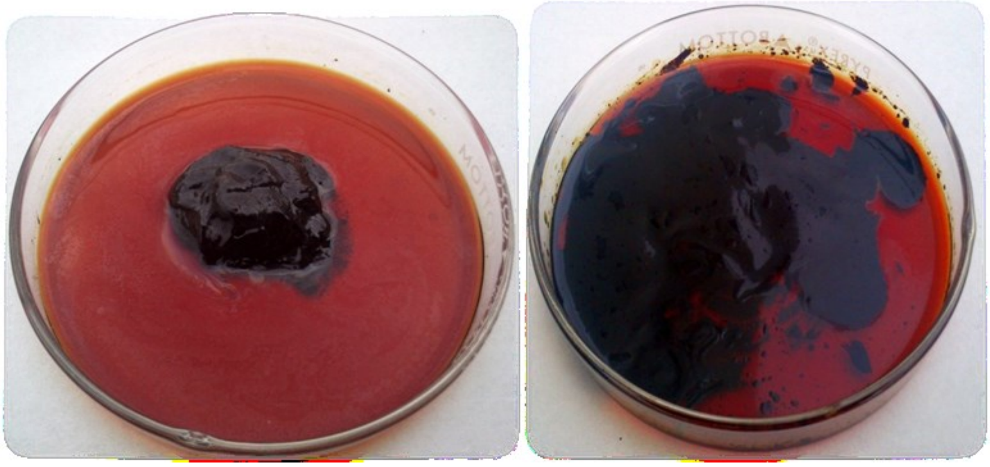


Figure 75: Effect of the temperature to the different phases of the oil. (10 °C on the left side and 25 °C on the right side)

6.6.2 Pyrolysis char

The solid products of the pyrolysis, also called char or coke, are collected in the coke collecting bin. Part of the coke remains in the reactor and is not discharged with the gas stream. This coke is mixed with sand, whereby this mixture is according after the experiments when the reactor is opened. The solid particles remaining in the reactor are not that homogeneous and do not have fine grain sizes like the one as those in the coke collecting bin of the cyclone. In Figure 76, the difference between the two types of char is shown.

Figure 76: Char from the reactor mixed with quartz sand (on the left) and char collected in the collecting bin (on the right)

6.6.3 Pyrolysis gas

After the gas flow passes the cyclone, the condenser, the different traps and the glass wool filter, the pyrolysis gas is burned. The composition of the gas was not determined in this

Thesis. Due to the flame, it can be assumed that the gas has a useful calorific value. The flame formation during the experiments is illustrated in Figure 77.

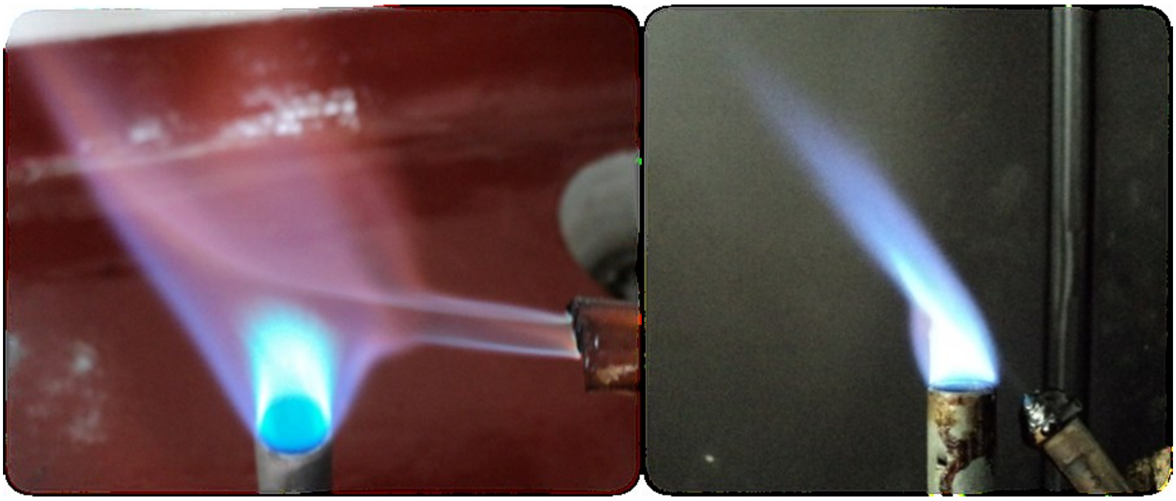


Figure 77: Flame formation by the combustion of pyrolysis gas.

7 Results and discussion

Investigations and recherches done in the framework for this work have shown that the energy demand in Peru will increase steadily through economic growth and rising prosperity. It was also found that there is an enormous potential for the generation of energy from different renewable sources. This potential should be used in the future as it will be a very interesting market. The Peruvian government is trying to promote the use of renewable energy sources with new laws and regulations. Now, it´s time to work hard and make big efforts for a successful implementation of these rules and chances. Due to low population density and locations with remote settlements, decentralized solutions for power generation are urgent and necessary for supplying the people with energy.

In addition, the great potential of energy generation from biomass in Peru is apparent. Large amounts of biomass wastes from agriculture and forestry remain so far unused and are not supplied to an efficient energy generation process. One of the reasons is the lack of know-how and technological equipment. There are only a few companies that offer technical solutions for energy recovery from biomass in Peru and little R&D work only is done in this area. The goal should be to develop and deliver customer oriented technology for Peru, processes that can utilize the specific types of organic wastes that are available in this country. Furthermore, the proved technology should be able to generate energy in a suitable form for Peru, for example, it is not necessary to use forestry wastes to produce heat for private houses (like in Europe) in the jungle region, it would be more recommendable to produce biodiesel. Another interesting solution, with reference to the problems of climate change, would be the production of fertilizer from biomass (like biochar, compost, etc.) in order to bind CO_2 for a long-term and in that way help to reduce the concentration of this greenhouse gas in the atmosphere.

In consideration of all these options and potentials in Peru, this PhD-Thesis was elaborated to make the first steps to investigate the topic of pyrolysis in Peru scientifically. The big advantage of this process is that different products (char, oil and gas) can be produced and also the utilization of different raw materials as feedstock is possible. The main objective of this work was to design and construct a pyrolysis plant and prove its functionality. In addition, some analyses of the products have been made and the results achieved were compared with literature.

In principal, it was proved that it is possible to design and construct a pyrolysis plant with indigenous materials and parts available on the national market only. Although until now there is still potential for improvements, **the first step was made**. In chapter 8, some recommendations for improvements and further investigations are given in connection with this work.

The following analyses and characterizations of the recovered pyrolysis oil presented in this chapter are intended to give a broad overview of the main features of this product and the possibility to compare the results with that of similar research projects. The aim is to draw conclusions and ideas for future research projects, experiments and improved methods for analyses. With the positive results achieved more possibilities for R&D-funding in Peru are hoped for, as the modest financial possibilities were one of the strongest limiting factors. As this is the first known pyrolysis plant for bio-waste in Peru, it was not possible to make direct comparisons within the country. It was also quite difficult to find external devices which can perform the specific analyses for these types of pyrolysis oils.

7.1 Experiments to determine effects on the product yields

The presented results are from pyrolysis experiments with coffee grounds. Also, preliminary experiments with rice residues (cooked rice waste from the cafeterias of the university) were performed, but with this material the reactor was plugged up very fast with solid residues (Figure 78) at different experimental conditions. In addition to coffee grounds, cooked rice showed the best preconditions among the tested raw materials to be used in a pyrolysis process. A relative high heating value and very low percentage of inorganic components seemed to be promising properties (see Table 18).

However, as already mentioned above, due to the problems with clogging the experiments with rice as feedstock were not continued in this first stage of the project. It is believed that because of the low cellulose and lignin content of cooked rice this feedstock is not really suitable, but for a further judgment and more exact answer, more experiments are necessary too.

Figure 78: Residues that plugged the reactor when using cooked rice as raw material feedstock.

7.1.1 Influence of pyrolysis temperature on product yields

These experiments should help to find the optimum pyrolysis temperature for coffee grounds. In different publications, the optimum pyrolysis temperature for biomass is between 475 and 550 °C [59] [60] [62] [76]; for that reason, 475 °C, 500°C and 525 °C were chosen for the first experiments. The average product yields of the experiment are summarized in Table 25 and depicted in Figure 79.

Table 25: Average percentage distribution of the product yields at different temperatures

	Average percentage of the product yields		
Temperature	Oil [wt%]	Coke [wt%]	Gas [wt%]
475 °C	39.9	20.9	39.2
500 °C	45.0	20.7	34.3
525 °C	38.0	17.1	44.9

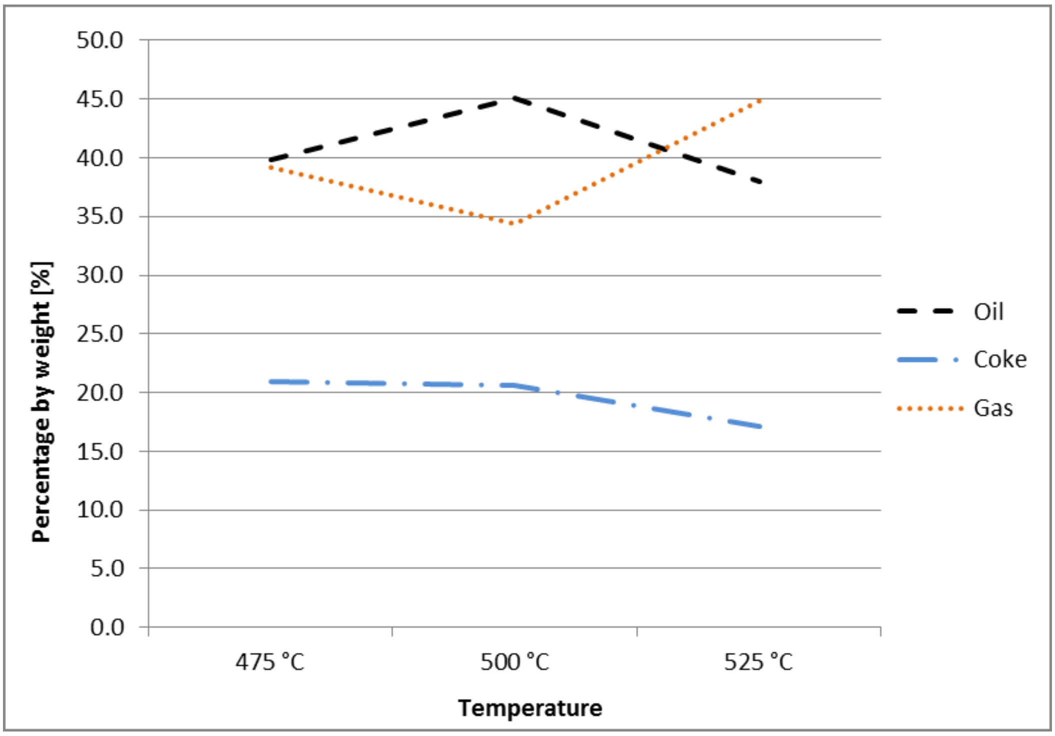


Figure 79: Product yields from the pyrolysis of coffee grounds at different temperatures

Figure 79 shows a typical course for pyrolysis yields at the applied temperatures. It was expected before, that the highest oil yield will be achieved around 500 °C. Also, the char production decreasing and the gas development rising are consistent with other research works [59] [60] [62] [76]. These curve progressions are quite typical for pyrolysis processes and can also be found in a variety of publications using different organic raw materials as feedstock. Data show that the **best pyrolysis temperature to get high oil yields** for this type of reactor with coffee grounds is **500 °C**.

Comparison of the achieved oil yield of 45 wt% with results of other pyrolysis research works show that the value obtained is far behind the values reported from pyrolysis of pure wood (up to 75% oil) as feedstock. Other pyrolysis experiments with coffee grounds as a raw material achieved product yields up to 55 wt% [76]. As this is the first pyrolysis reactor “Made in Peru” and this kind of research in Peru is still in its infancy, the lower oil yields are not a big surprise or disappointment either. In chapter 8 some recommendations are made to improve the PUCP-pyrolysis plant to get a higher product yield.

7.1.2 Different gas flows

Another important process parameter for pyrolysis is the gas flow. The retention time of the products in the reactor depends strongly on this operation parameter. One of the problems is that factors, like minimum fluidization velocity and retention time, can be calculated theoretically but during the process the gas is heated up and also new gases are built in the reactor. These practical difficulties only permit limited prognoses on the optimum gas flow. For that reason, it is important to make more and different experiments to verify the effects.

A very important gas flow parameter is the **minimum fluidization velocity**. For the PUCP-pyrolysis reactor the minimum fluidization velocity is 0.17 m/s (equivalent to 1.2 m^3/h at 20 °C) which was verified with the reactor model. It must be kept in mind that during the experiments the temperature becomes very high and the gas expands. The coefficient of expansion for N_2 is 0.003674 per Kelvin, which means the gas grows from 20 °C to 480 °C by the factor of 1.76 so the necessary gas flow decreases by that factor.

For the experiments, a gas flow of 10 L/min, 12.5 L/min and 15 L/min respectively and a pyrolysis temperature of 500 °C were chosen. The results are summarized in Table 26 and in Figure 80.

Table 26: Average percentage distribution of the product yields at different gas flows

	Average percentage of the product yields		
Gas flow	Oil [wt%]	Coke [wt%]	Gas [wt%]
10 L/min	40.7	18.1	41.2
12.5 L/min	41.6	19.8	38.7
15 L/min	42.4	20.4	37.2

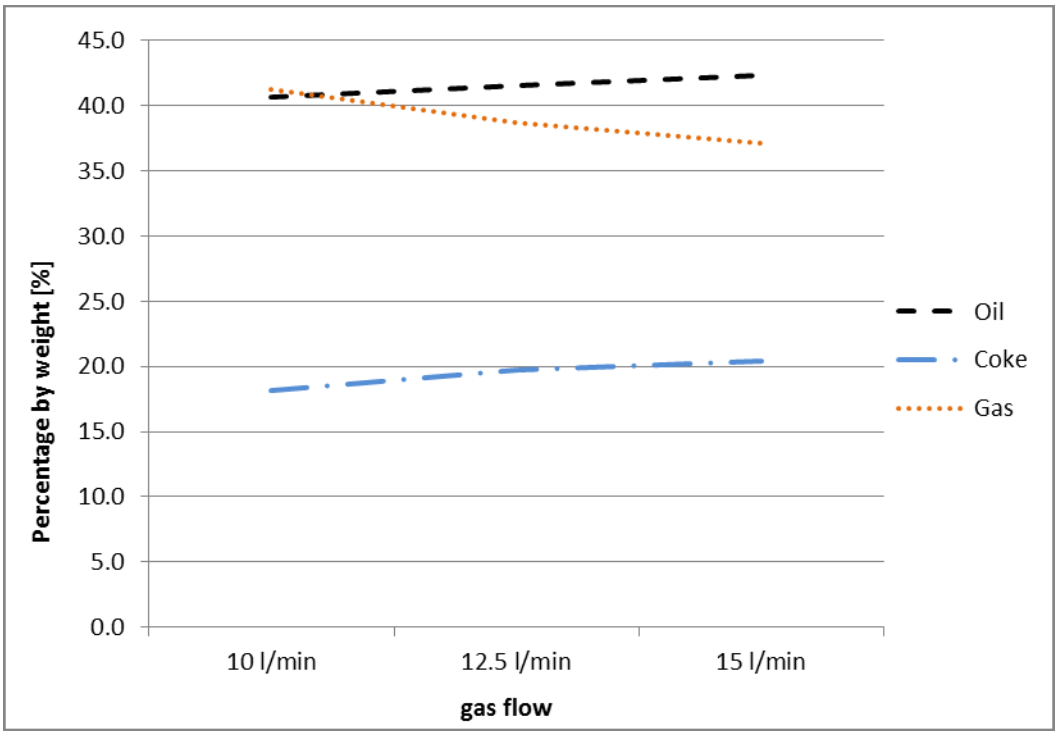


Figure 80: Product yields from the pyrolysis of coffee grounds at different gas flow rates [L/min]

These experiments show that the influence of different gas flows between 10 and15 L/min is not very big but a light increase in oil product yield could be observed. The observed decrease of the pyrolysis gas yield can be explained by lower retention times in the reactor. It is assumed that with some more experiments, including gas flow rates up to 30 L/min, it would be possible to make more accurate statements and conclusions. A question that must be solved in the near future is, at what gas flow rate the quartz sand bed material is leaving the reactor. To answer this it is necessary to exam the biochar collected in the coke bin of the cyclone to see if there are also sand particulates collected. One factor which was not considered is the production of gases during the reaction which also has influence on the gas flow and the retention time.

The production of coke was rising softly with higher gas flows. This can be explained with a better and higher discharge of solid particles out of the reactor.

7.1.3 Different amounts of raw material feedstock

The goal of these tests was to investigate if the use of higher amounts of coffee grounds feedstock has an influence on the product yields. The results are summarized in Table 27 and in Figure 81. It is assumed that during long term experiments the plant is better heated up so the temperature will be more stable. On the other hand, the deposits on the walls can increase with time which can lead to a blockage, and there is also an increase of the fluidized bed material because not all of the coke particles are discharged.

Table 27: Use of different amounts of coffee grounds as feedstock

	Average percentage of the product yields		
Raw material input	Oil [wt%]	Coke [wt%]	Gas [wt%]
200 g	41.2	26.5	32.3
300 g	42.6	19.7	37.7
400 g	47.8	17.0	35.2

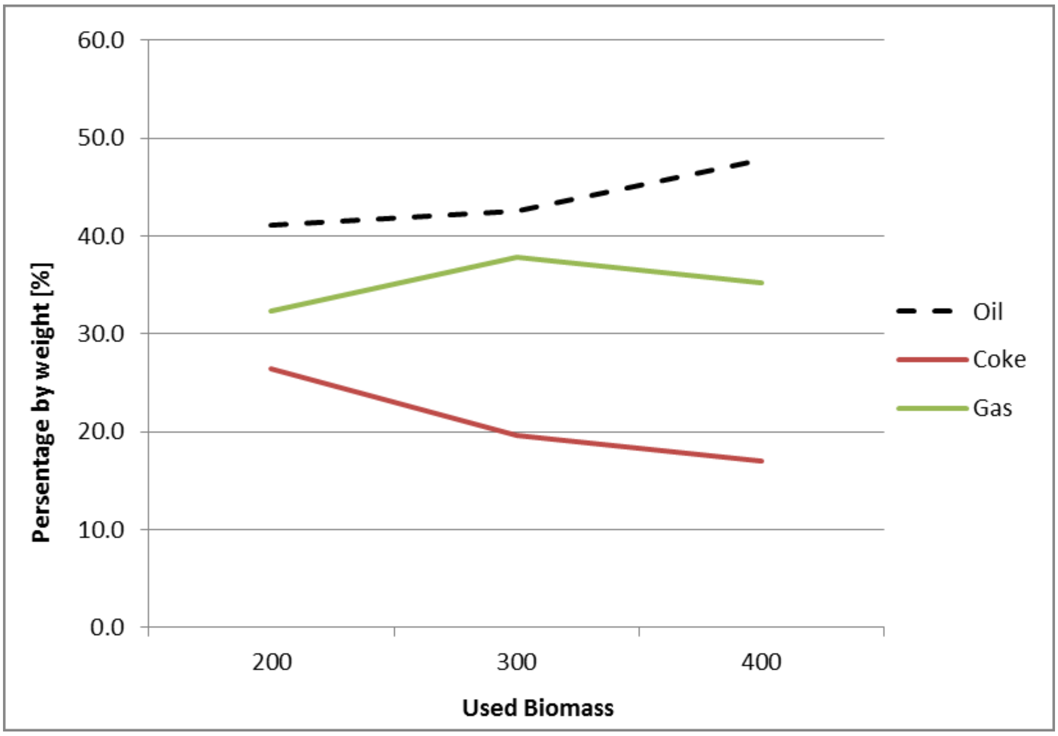


Figure 81: Product yields using different amounts of biomass feedstock.

Figure 81 shows clearly an increasing of oil yields with larger amounts of feedstock or longer process duration. It is assumed that this is the result of more stable temperature profiles in the total plant. Due to the longer stay of the coke particles in the reaction zone (500 °C), they have more time to react, which results in an increase of the oil yield and a decrease of the char yield.

7.2 Characterization (physical and chemical) of the pyrolysis oil

Regarding the main product, the collected pyrolysis oil forms two different liquid phases that can be separated as shown in Figure 73 and Figure 74. The lighter phase is a dark liquid which is more viscous than the heavier one. The analysis results show that the heavy phase contains a high amount of water, which is the reason why only a few analyses have been done for this sample. The heating value (HHV) of the lighter phase can be doubled by the simple step of phase-splitting., and is nearly like domestic fuel oil (43 MJ/kg) or gasoline (41 MJ/kg). This means that the pyrolysis technology applied raises the energy density of the feedstock. Analyses data present low sulfur and inorganic mass contents. Density was measured in an extern laboratory and also by using a pycnometer (Pycnometers, Blaubrand®, with thermometer and side capillary, Borosilicate glass 3.3. DIN ISO 3507, Guy-Lussac type) and was determined with 1.038 kg/m^3.

The results from the pyrolysis oil analyses are shown in Table 28 and Table 29. **Table 28** shows the results of the entire oil (both phases together) and it can be observed that the water content is over 25 Vol%, which is consistent with the values found in the literature [45]. Very low sulfur content and low ashes percentage indicate that the investigated oil sample composition is mainly organic. The heating value (HHV) is higher than for wood (about 15 MJ/kg) but lower than for domestic fuel oil (43 MJ/kg).

Other investigations show similar results with a density of 1.1 kg/L, ash content smaller than 0.2 wt% and a heating value (HHV) around 20 MJ/kg for the entire oil [76]. Due to its property for building two different phases, the oil was put in a separation funnel for splitting into two phases. These phases were analyzed separately and the results are shown in Table 29.

Table 28: Measured parameters of the entire oil

Method	Parameter	Unit	Oil
ASTM D 95 / 05 (10)	Water content	% Vol	> 25
ASTM 1298 / 99 (05)	Density	kg/m^3	1,038
ASTM D 4868 / 00 (10)	Heating value	MJ / kg	17.39 (LHV_{OS}) 19.72 (HHV_{OS})
ASTM D 482 / 07	Ashes	% mass	0.028
ASTM D 4294 / 10	Sulfur	% mass	0.201
ASTM D 92 / 12a	Flash point	°C	*

ASTM D 97 / 11	Pour point	°C	+ 18°C

* not measureable because of high water content.

Table 29: Measured parameters of the two separated phases of the obtained oil

Method	Parameter	Unit	Light Phase	Heavy Phase
ASTM D 95 / 05 (10)	Water content	% Vol	11.0	>> 25
ASTM 1298 / 99 (05)	Density	kg/m^3	1,027	1,058
ASTM D 445 / 12	Viscosity	cST	*	*
ASTM D 4868 / 00 (10)	Heating	MJ / kg	35.48 (LHV_{OS}) 37.74 (HHV_{OS})	---
ASTM D 482 / 07	Ashes	% mass	0.035	---
ASTM D 4294 / 10	Sulfur	% mass	0.163	0.0685
ASTM D 92 / 12a	Flash point	°C	*	*
ASTM D 97 / 11	Pour point	°C	+21	

* not measurable because of high water content.

The results show that some of the investigated parameters could not be measured with sense because of the high water content of the products obtained. Compared to the results of Jin *et. al* [76] the physical and chemical characteristics of the pyrolysis oil are very similar. Nevertheless, better methods and ways have to be found to analyze the oil and compare it with literature data and with other raw materials feedstock.

7.2.1 FT-IR Spectroscopy results

FT-IR spectroscopy was applied to samples of both fractions of the recovered pyrolysis oil. The spectra were obtained with a FTIR Spectrum 100 Perkin Elmer spectrophotometer, thin oil film between NaCl windows, and resolution 4 cm^{-1}. The two spectra of the different oil fractions showed the same profile as in Figure 82.

Figure 82: FTIR Spectrum of the entire oil sample

O-H stretching vibrations between 3,200 and 3,400 cm^{-1} corresponding to presence of **phenols** and **alcohols** are observed. There are C-H stretching vibrations also between 2,850 and 2,950 cm^{-1}typical for **alkanes**, and C-H deformation vibrations can be found between 1,350 and 1,475 cm^{-1}. Also presents are bands at 1,378 and 1,453 cm^{-1} for bending vibrations of C-H groups as well as C=O stretching absorptions at 1,704 cm^{-1}, possibly due to saturated open chain **ketones**, **aryl aldehydes**. There is a visible band at 1,514 cm^{-1} that could be assigned to aromatic C=C ring vibrations, *i.e.,* **aromatics with various types of substitution**. At 1,200 and 1,300 cm^{-1}, C-O axial asymmetric deformations bands are present. [79] [80] [81]

7.2.2 GC-MS Chromatography results

To analyze the oil samples by **chromatography** and by **GC-MS** they have to be solved in pure volatile solvents first. For this purpose, preliminary tests were made to try different analytical grade solvents and mixtures of them. The used solvents were:

- Methanol
- Ethanol
- Acetone
- Dichloromethane

The best results were obtained by using a mixture of 50 Vol% of acetone with 50 Vol% of dichloromethane. For the other solvents tested, the oil samples did not totally dissolve; in other cases, floating particle clouds could be observed. In the described mixture of acetone with dichloromethane (50:50) both phases of the oil were dissolved so this mixture could be used for GC-MS.

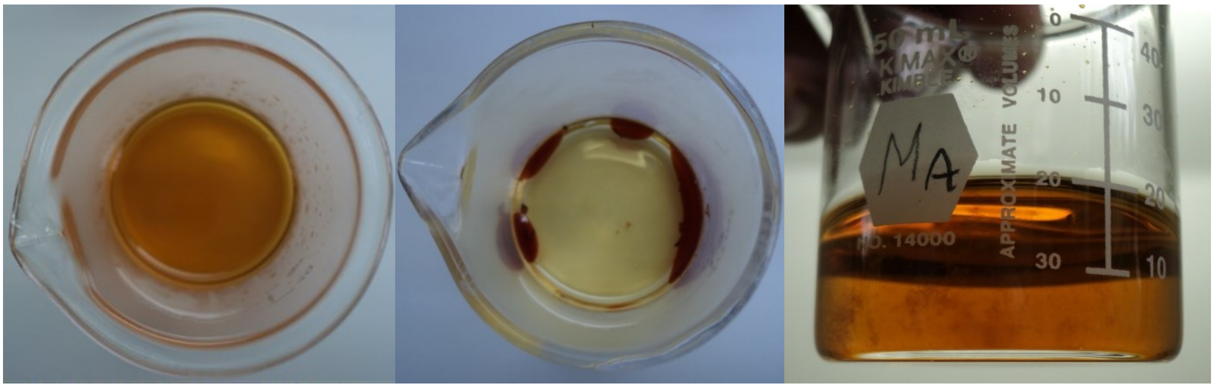


Figure 83: Sample preparation for GC-MS: Preliminary dissolution tests with different solvents: satisfactory dissolved oil (on the left), not dissolved oil (in the middle) and partly dissolved oil with floating particle clouds (on the right).

For **gas chromatography**, a HP 5890 Series II GC with a HP-1 (Methyl Silicone Gum Instrument Test, 5 m x 0.53 mm x 2.65 µm film thickness and PetroCol 2887 Crosslinkeddimethylpolysiloxane Capillary Column, 5 m x 0.53 mm x 0.1 µm film thickness) was used. The program features are:

- Injection temperature: 340 °C
- Detector temperature: 350 °C.
- Initial temperature: 40 °C for 5 min
- Final temperature: 330° C for 5 min
- Heating Rate: 8 °C/min
- Sample volume: 1 µL
- Gas (gas flow, pressure): He (5 mL/min, 2 psi)

Supelco C8-C20 and C8-C40 alkanes calibration standard in dichloromethane mixtures were used. It was possible to identify **alkanes with 15, 17, 18, 19 and 28 carbon atoms** for the light phase, and **15, 17, 18, 20, 25, 28, 31 and 33 carbon atoms** for the heavy phase (Figure 84).

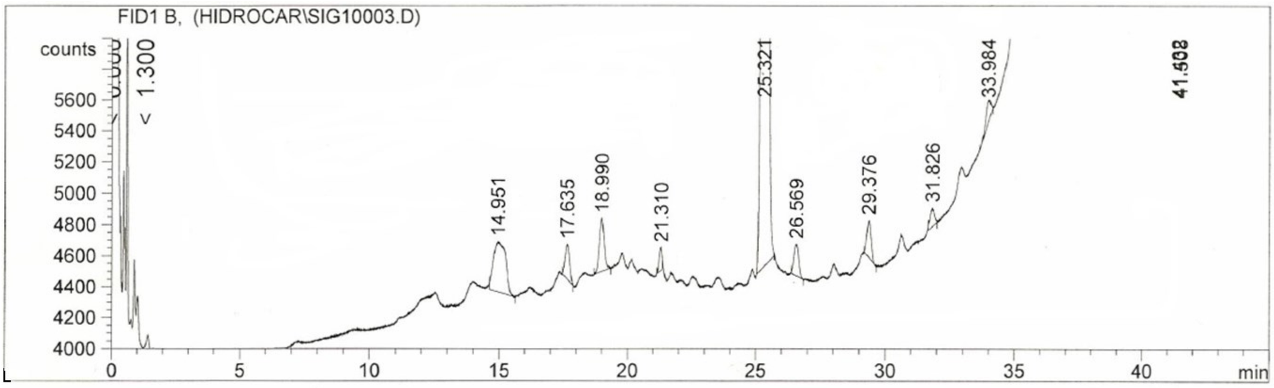
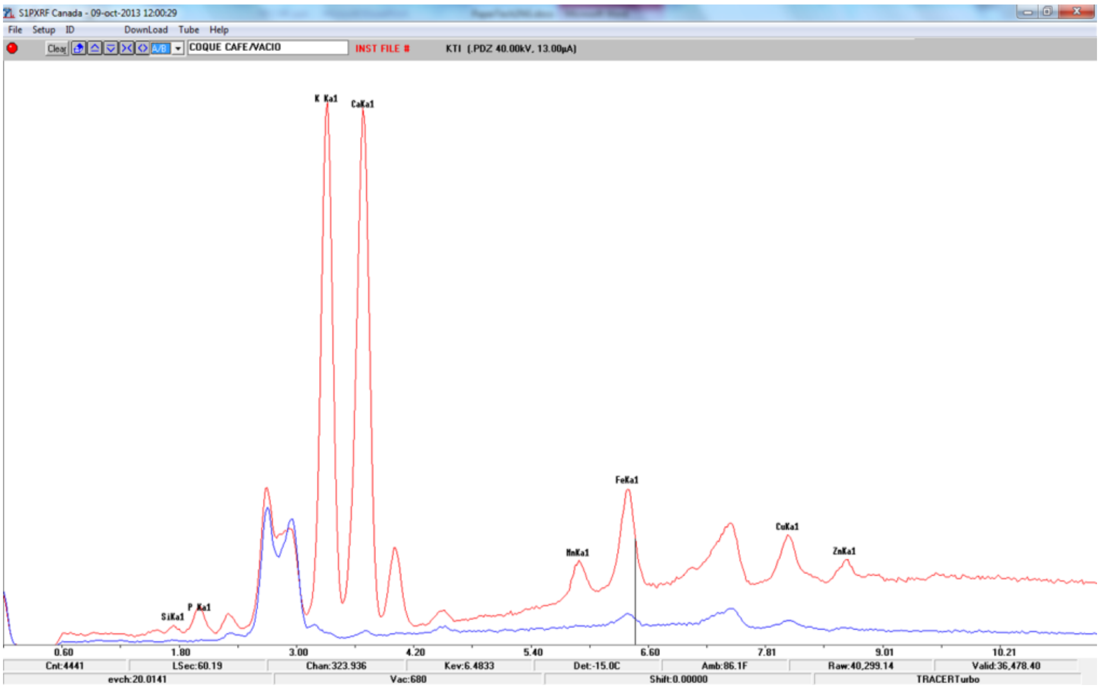


Figure 84: GC-MS Chromatogram of bio-oil sample (heavy phase)

As a result of the literature research done, it was expected, that more carbon compounds would be present in the oil samples that could be identified by the GC analysis. In the research paper by Jin *et. al* [76], for example, over 40 different organic compounds were identified in the pyrolysis oil obtained from coffee grounds. Further studies with different solvents seem to be necessary to clean this discrepancy. In additional tests, the influence of different instrumental parameters of the GC has to be checked, to secure the identification of all relevant organic compounds of the oil.

7.3 X-Ray Fluorescence Spectroscopy of the recovered biochar

X Ray fluorescence spectroscopy was applied to coke obtained from the coffee grounds by pyrolysis (Figure 85) using an ED-XRF Bruker AXS Handheld model and sample cups with Mylar® thin film. The samples were kept in a desiccator and analyzed under laboratory conditions, 40 keV, 60 s run, without filters, under air for the 100 % method. The composition (Figure 86) for clear identified elements was calculated using the main peaks. XRF indicates that **main elements** present **in coke** are **K** and **Ca** (> 70 %) and transition metals (F**e, Ni, Cu, Mn, Zn and Ti**) reaching almost 25 %. This result agrees with data known from the literature.



S1PXRF Canada - 09-oct-2013 12:00:29

COQUE CAFE/VACIO

INST FILE #

KTI (.PDZ 40.00kV, 13.00µA)

Cnt:4441 LSec:60.19 Chan:323.936 Kev:6.4833 Det:-15.0C Amb:86.1F Raw:40,299.14 Valid:36,478.40

evch:20.0141 Vac:680 Shift:0.00000 TRACERTurbo

Red line: coke; blue line, XRF sample cups and Mylar film, no sample

Figure 85: EDX-Ray fluorescence spectra of coke obtained from coffee grounds by pyrolysis

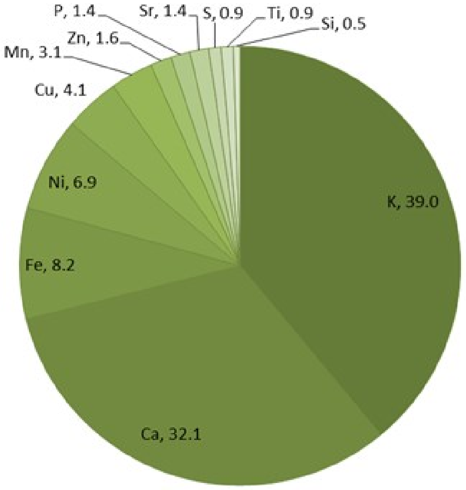


Figure 86: Relative elemental percentage composition for recovered pyrolysis coke by ED-XRF spectroscopy

7.4 Set up of the plant and discussion of shortcomings

7.4.1 First section of the plant: charging hopper - reactor

The goal of this work, documented by the PhD-Work was to build a small pyrolysis plant in Peru and to start R&D activities on the subject of renewable energy from biomass and bio-wastes in the country. This PUCP-pyrolysis plant should be built only with materials which are available in Peru. These objectives could be fulfilled and also first results and analyses of the recovered products are proving the feasibility of the R&D idea and concept. As the PUCP-pyrolysis plant is the first reactor of this type in Peru, no experiences were available; some parts of the plant have been made after an often used model based on the **"Hamburger Wirbelschichtverfahren"**. Research works with different input raw materials (like: rice straw, coffee grounds, wood, plastic wastes, etc.) were performed using this type of reactor. Nevertheless, there were quite some things that did not worked as planed and unforeseen incidents occurred. In this chapter 7.4, the technical problems will be discussed and in chapter 8 some recommendations for improvements are elaborated.

To start with a simple, but troublesome problem: The discharge of the biomass from the storing tank was not working well. Especially, when the biomass was not dry enough, the problem became real tedious. The reason for that is a small hole at the bottom of the storage tank and the relative steep angle of the walls. Another short come is that the rotary valve is not directly connected under the storage tank. All these points together can lead easily to a bridging of the raw material. When that happens, the material flow must be reestablished by gently tapping on the storage container. Also, the gas flow or the pressure can be increased for a short time in order to release the blockage. In future, the installation of a simple agitator could be a promising way to solve this problem. Also the lid of the charging hopper was not completely tight; over here certainly better solutions must be found to minimize the loss of nitrogen.

In the next step, the amount of biomass (i.e. how many biomass enters the reactor), is regulated by the rotary valve. This option to regulate the biomass flow is a very exact and easy controllable measure. This part of the plant is very reliable and can be easily cleaned. The only disadvantage is the selected small size of the rotary feeder. This may result in constipation when wet raw material feedstock is used; furthermore, the particle size of used biomass is strict limited. An essential improvement would be if the rotary valve and the screw are driven by two different motors; a motor with variable speed is advisable for the rotary feeder. It is particularly important that the biomass entry is controlled by the engine speed and the screw transports the biomass as quickly as possible into the reactor, so there is no incrustation or hard shell formation of the feedstock material by heat which affects the reaction in the reactor negatively. The existing system has only one motor for both parts. If only a small biomass flow is desired now, a very low motor speed is needed which also leads to a slower rotating screw conveyor speed and a slower entry speeds. A higher entry speed would make an additional cooling system unnecessary.

In general, the diameters of the installed connecting tubes are too small, thereby the clogging formation is facilitated and the particle size of raw materials input is very limited.

The installed conveyor screw worked well and was also resilient enough. Despite obstructions and thermal stress, there were no bends or other deformations visible. Still, some thoughts should be given to improvements in the design of the feeding screw, to be more flexible for different raw materials and to prevent clogging.

All rotating parts of the plant have the problem that they are not 100% sealed and losses of nitrogen or process gases are the consequence. The system used in this PUCP-pyrolysis plant to reduce the gas losses to a minimum could decrease the problem to an acceptable level. In order to quantify these still existing losses, it is necessary to install a gas meter at the beginning and at the end of the process. An analysis of the gases was not made in this stage of the project, because until now no facility was found in Peru which can make this kind of analyses and suitable instruments have not been available at PUCP.

The reactor worked flawlessly. One smaller problem was that quite a lot of char particles remain in the reactor and a mix of coke and sand particles is formed in the reactor. This mix had to be taken out of the reactor from time to time and new sand had to be added as bed material. The spent sand can be regenerated and reused by first heating it in a furnace to a temperature of more than 750 °C, followed by washing and drying it.

The reasons for the low discharge of char could be either bad flow conditions in the reactor and/or a too thin connecting tube between the reactor and the cyclone. The rather small diameter of this tube was chosen, expecting that it will cause an increasing of gas velocity, leading to a better discharge out of the reactor and a better separation in the cyclone. However, it has been found that deposits (crust formation) on the walls in this tube are formed quickly, which can cause blockages. Therefore, the reactor must be disassembled from time to time and cleaned. Also, on the cover blade of the reactor (Figure 87) accumulations (deposits) of solid and liquid products were found after the experiments. These sediments have to be removed before next test. For a final solution of this problem, the discharge zone of the reactor needs to be redesigned in order to allow a better and easier discharge of the products and to reduce deposition.

Figure 87: Deposits formation on the reactor cover blade

There are altogether 3 measuring points for temperature in the reactor combined with a temperature controller and a system to save the data on a memory card. This system was built together with an undergraduate student of the Faculty of Sciences and Engineering of PUCP, but was running unsatisfactorily. Therefore, the measured data could not be recorded electronically. The thermocouple in the fluidized bed was connected to the controller to regulate the reaction temperature and the other measuring points were used to check the temperature.

The metal mesh of the reactor bottom prevented the sand of the fluidized bed to flow out. After about 20 experiments, this metal mesh had to be renewed. The heating system of the reactor reached the desired temperature in a relative short time, but during the experiments it was found, that the control system reacts a little bit sluggish, whereby a slightly higher temperature value was necessary to adjust on the controller to maintain a fluctuation range of +/- 10 degrees of the desired temperature only.

7.4.2 Second section of the plant: cyclone – control filter

Calculations have been accomplished with general parameters to design and construct an universal cyclone, since nothing about the properties of the particles, which have to be separated, were known at the beginning. In comparison with similar pyrolysis research projects, the finally built cyclone is bigger. Considering the specific properties of char particles a more appropriate cyclone could be built. Another possibility would be the installation of a second cyclone after the first one. However, a higher heat loss would be the disadvantage. A fair compromise could be the installation of two smaller cyclone units, so that the surface would be less and therefore the heat losses too, and at the same time, a better separation efficiency for solid particles from the gas stream could be obtained. The collection bin of the char is definitely too small; it should be increased in any case.

The connecting tube between cyclone and condenser (Figure 88) turned out to be a weak point of the system. The length of the tube was causing increased heat losses and deposits (losses) on the wall of the tubes. Length and shape of this component was chosen to compensate thermal expansion of the metal parts of the plant to avoid tensions or material fractions of glass parts. After the first experiments it turned out, that the system expands only negligible by high temperatures. To minimize the loss of material in the pipe as well as the heat losses, a shorter tube may be used. The connection between metal and glass worked very well, but the screws have to be tightened very carefully so that the glass of the condenser will not break.

Figure 88: Connecting tube between cyclone and glass condenser

The condenser and the remaining parts of the PUCP-pyrolysis plant for the products separation worked very well. The last control filter before gas-combustion discolored during the experiments relatively quickly from previous white to dark brown, which suggests that not all of the solid and liquid particles dispersed presented in the gas are separated. Through additional separators (*e.g.,* electrostatic precipitator) the separation has to be improved in the future.

7.5 Discussion on research activities and related challenges in Peru

Research and development (R&D) in the technology sector of a developing country differs in many ways from R&D in a developed one. Main differences exist in the organizational, financial and material areas. Nevertheless, it would be very important for the growth in emerging markets that **clean and new technology** is developed and available in the country as well as **trained manpower**.

In general, there are manifold problems, although some of them could be solved directly by research facility and researches. The others have to be solved by government, other public institutions and society through time and may take several years, perhaps generations.

When international researchers want to undertake research in one of these development countries like Peru also the residence authorization may be a stone in the way. It has to be checked if an official visa for researchers exist and what are the necessary documents and steps to get one. Peru, for example, until now does not have a special visa for researchers, the only way is to stay as student or as worker with a working contract.

7.5.1 Organizational challenges

Before starting a scientific project in a developing country, different things have to be considered. Communication is one of the most important things, whereby it is necessary to be familiar with the local language, at least at base level as it is not sure at all that people have basic knowledge in English. Maybe for the laboratory research at university English is enough, but for all the things necessary around the research project (organization of equipment, buying of equipment and machines, transport, etc.) it is very helpful to understand the local language.

In many developing countries, the difficulties and high costs of importing scientific research equipment or spare parts can lead to severe problems. To have to overcome a lot of bureaucracy for permissions and long waiting times at the customs duty office can be expected as normal. On the other hand, it is difficult to find sophisticated and high quality scientific equipment which is produced in the country itself. Also, it is not easy to find out where the desired devices and items are available and can be bought. In Peru, for example, there is only very less information over internet available and ordering online is not common at all. It is necessary to invest a lot of time to ask and go here and there to find the needed products. In quite some cases, the required materials or equipments are not available, so new solutions must be found and/or improvisations have to be made.

For a successful R&D-work, a strong local partner (university, research institution, company etc.) with good facilities is a must. An advantage is, when the local establishment can count on a good international network.

Another weak point in developing countries is the missing connection between university and industry. There are only a few positive projects where joint synergies are used, although there is a lot of development potential. To strengthen this cooperation, a relationship of trust between both has to be established and both need to be aware of the enormous benefits of such cooperation.

7.5.2 Financial and human resources challenges

To find funding for R&D-work in developing countries is a big challenge. Nobody can expect support just coming by itself. People who have the money and also members of the government, in most of the cases are not scientists and a lot of awareness training has to be made. Also, priorities in developing countries are very different from ours. Mostly, governments have to fight against basic problems like illiteracy, poor school education, poor infrastructure, corruption, etc. So, resources available are used to meet and secure basic needs. In the case of this research work, the project behind the PhD-work was financed by the PUCP, where students and professor can present projects to get financial support. But even though, if there are funding possibilities, the amounts are much lower than, for example, provide for comparable projects in Europe or the USA. An important point is, if some money for a project was obtained to work hard on getting results and present them. Nowadays, there is also international funding available in Peru that can help to finance interesting projects.

For high quality research, also a team of qualified persons is necessary, whereby the basis of educated people is much smaller than in developed countries and, especially in the area of new technologies, there are hardly experts or trained personal available. This problem may be solved by long term projects where the status and facilities in the country could be improved. Nevertheless, the most qualified and interested scientific man power should be selected, whereby motivation and interest of the people is a very important point, like anywhere else.

8 Conclusions and recommendations

8.1 Conclusions

This R&D work has proven that it is possible to develop new technologies in Peru for using organic waste materials as an energy resource. The described pyrolysis pilot plant was constructed at PUCP in Peru only with materials and parts available in the country and worked satisfactory. It is clear that the development of this technology only is at its beginning in Peru. But the first results are promising and do match other international research works.

The investigated coffee grounds were a suitable feedstock that needs little preparation only before pyrolysis. This raw material is also easy available and as an organic waste that can be found all over Peru and in the whole world. Until now, mainly experiments with coffee ground were made which worked out well. Also rice waste was used as feedstock but the results achieved did not meet the expectations so far. In the next step different, organic wastes (typical for Peru) will be tested in the PUCP plant to determine their potential for energy generation. An example would be the use of rice husks, which are available in Peru in large quantities from the production of rice. This bio-waste so was is not utilized

The PUCP-pyrolysis plant has worked quite well during the first series of experiments. The pyrolysis plant, being at the present state of knowledge, is the first and to date only the one of this type in Peru. All the parts of the plant could resist the high operation temperatures and could be repeatedly mounted and dismounted without loss of function. The good isolation and heating system can heat up the reactor very fast. Also the cooling-traps and filters worked very well and showed the expected results. However during the experiments, also potentials for further improvements were found. Large modifications of the existing reactor do not make sense, as it would result only in modest improvements at high costs. Therefore a scale up of the equipment (for example to handle up to 1 kg biomass per hour) and the construction of a larger plant is recommended. In the following sub chapters, some recommendations which should be considered for the construction of a new plant and also recommendations for further experiments are given, to create a better understanding of the process and to find the best methods to analyze and characterize the output streams of the pyrolysis process.

The focus on this work was to produce pyrolysis oil. The yield of the liquid product from the pyrolysis process was over 45 % (i.e. up to 47 %) and it is assumed that with some modification on the plant, even higher yields can be achieved. The heating value (HHV) of the recovered oil was nearly 38 MJ/kg_{OS} which is a little bit lower than the calorific value for fuel oil (~ 45 MJ/kg) and it shows the possibility of converting biomass into a secondary raw material with higher heating values.

The first analytical results of the investigated oil showed a low content of sulfur and inorganic compounds (ashes) which are desirable properties for fuels. Also the results of the GC-MS analyses show typical hydrocarbons and other organic compounds that are common for pyrolysis oil. But it is clear that the methods for the analyses of the oil have to be improved in the future as a complete characterization of the recovered product is necessary for comparison with traditional standard oil qualities.

The produced gas was burned only without a detailed analysis. Due to the type of flame observed it can be concluded that this gas may also be used for generating energy. It is therefore essential to analyze the composition of the pyrolysis gas in the next stage of the project. The obtained char was very fine, homogeneous and pure. This product should also be analyzed more intensively in future and an evaluation of the possibilities for utilization has to be done (for example: as activated carbon, fertilizer, etc.).

As already mentioned before, the produced biochar has a very fine and homogeneous granulation which means a large surface. The observed problem was that quite a lot of biochar stayed in the reactor and was not separated by the cyclone. When the reactor was opened after the experiments, the coke–sand mix was taken out, but it is not such a pure biochar like the one which got collected in the cyclone.

The described PUCP-pyrolysis plant has not produced residues during the process. All the biomass is converted into gas, biochar or oil. In the cleaning process, spent sodium hydroxide is remaining which has to be recycled. Also the isolation and sealing material of the equipment had to be exchanged from time to time which caused some solid residues.

8.2 Recommendation for technical improvements

In Peru, there exists an enormous, so far untapped biomass potential, especially as far as improved utilization of existing residues of the agricultural and forestry industries is concerned. Use of new technologies and ways for bio-energy generation could bring social, environmental and economic benefits in rural and also in urban areas. A good integration and administration of biomass energy systems can stimulate eco-friendly sustainable development. To reach this goal, a sustainable economically justifiable production process must be provided.

In the future, it is expected that the global demand for biomass will rise considerably because of a higher energy demand in the developing countries and a greater use of renewable energies in industrialized countries.

The following suggestions in this chapter are mainly focused on building a new and larger pyrolysis plant by up-scaling of the existing PUCP-pyrolyzer.

An important issue of the pyrolysis process is the control of charging the right amount of material feedstock. Due to the reported smaller problems with the continuous flow of biomass (bridge formation) and to avoid tedious knocking on the container wall, the reservoir should have a larger discharge mouth and the walls a steeper angle to secure a continuous flow without problems. Also the connection tube between the charging hopper and the rotary valve should be shorter and with a larger diameter. Another possibility would be to attach the rotary valve directly under the charging hopper. The chambers of the rotary valve should have a larger volume so that different particle sizes of feedstock can be used in the experiments.

As already mentioned before, one of the most effective improvements would be the separate operation of the rotary valve and the screw conveyor, with 2 different motors. If lower amount of biomass feedstock per hour is needed, the low motor spins required for the rotary valve would not affect the entry velocity of the biomass in the screw driver, where a higher velocity is important to avoid encapsulation (formation of hard outer crusts) of the biomass particles. Furthermore, the two equipments independently can be turned off and on whenever there is a risk of clogging or blockage. The connecting tube between the two parts should have a larger diameter and be as short as possible.

For a scaled up larger pyrolysis plant also the screw conveyor has to be designed new. Therefore it is recommended to design smaller pin and a larger ratio between the flight outside diameter and shaft outside diameter to assure an impeccable functioning for different types of biomasses. For using also the gravity, the screw conveyor can be installed slightly sloping in direction to the reactor.

In the reactor, less thermocouples may be installed. The one in the reaction zone is important to control the temperature of the reaction and this one must be installed in any case. Depending on the length of the new reactor, the number of thermocouples has to be defined. A new design of the reactor head would be important to improve the discharge of different products and to avoid the accumulation of solids and liquids at the walls of the reactor. To test different systems, this part could be connected with a flange to change different options of reactor heads. This modular construction system would allow testing different solutions with one plant only. The connection tube between the reactor ant the cyclone should have a larger diameter to avoid excessive clogging.

The heating system worked quite well, only the control has to be improved. One promising option is to encapsulate all the high temperature parts (reactor and cyclone) with a kind of furnace. With this solution, also the isolation would be unnecessary as uniform temperature maintains in the whole burning chamber. There would be no more heat losses. The temperature profile during the experiments would be stable with fewer fluctuations which allow a more precise control of the pyrolysis temperature. The unnecessary insulation had not to be replaced and the safety at wokr would increase.

The cyclone installed worked quite well, but with the collected information and the experiences gained a more efficient one could be designed. To collect the biochar, a bigger collection container is recommended. In order to achieve a maximum degree of separation, the use of two cyclones can be considered, as long as the heat loss is not too much.

The whole process control system needs to be improved. In the first stage of the project it was tried to connect the measurement devices to the computer to store the data, which never did work well. Also a measuring device for the gas flow at the end of the process was missing in the first experiments. To overcome this problem, sensors for analyzing the gas composition during the experiments could be installed. But the best solution would be to connect all different measuring points directly with the computer and feed the data into a program where these values can be monitored during the experiments and also stored.

Product separation of the reactor output could be increased by additional electrostatic filters (ESP) installed after the condenser. These filters can be used for separation of both solid and liquid components. Another option would be the installation of additional cooling traps, but these are not as effective as electric filter.

At the end of the process line, before the gas is burned for disposal, a device for gas sampling should be installed. In a new plant, the possibility of using the gas to provide process temperature should be reconsidered. The use as a process gas after burning could be of tremendous advantage. In such a closed system, nitrogen carrier gas would be used only for starting up operation, and then a closed circuit would formed by using the burned gas as fluidization gas. Such a system would have a very positive impact on the energy balance of the pyrolysis process, resulting in economic benefits

8.3 Recommendations for further investigations

As the main objective of the PhD-Thesis was the design and construction of the reported PUCP-pyrolysis plant, only limited time was available for the investigation of process parameter, raw materials feedstock and pyrolysis product. There are quite a lot of parameters more that influence the pyrolysis process which have to be tested. In the same way, better and new methods have to be found to characterize the different products. These are important points for a better understanding of the whole process that will help to find out how the empire potential of this technology can be used in Peru.

Due to the lack of real reliable data, that could not be generated during the first fundamental experiments described in this Thesis, the establishment of **energy balances** as well as **materials balances** for the pyrolysis process have been postponed to the next step of the project, when the **new modified pyrolysis plant** is in operation.

8.3.1 Raw materials feedstock

Until now, only coffee grounds were used in the pyrolysis process as feedstock. The next steps would be to carry out a systematic search on organic wastes in Peru which can be used in the reactor, whereby cooperation with the industry would be recommendable. Different feedstock could be tested in the reactor to evaluate the qualification for pyrolysis.

It is also necessary to analyze the selected feedstock to know theirs composition. With these data and the data of the analyzed products, a forecast about the reactions in the reactor can be made.

Having collected enough data on the characterization and properties of different feedstock materials, it will be possible to decide about the utilization of the material.

8.3.2 Experimental parameters

A pyrolysis process is influenced by various parameters. The most important are temperature, gas flow and raw material properties. The following Table 30 provides an overview of the parameters whose influence has to be tested; also the interaction of different combinations of them should be investigated.

Table 30: Experimental parameters which influence on the process should be tested in the future

Parameter	Factors of influence
Gas	• Type of gas

	• Gas flow (residence time) • Pressure
Quartz sand	• Particle size • Amount of sand
Feedstock	• Composition • Particle size • Amount of material feed • Pretreatment
Temperature	• Temperature in the reactor • Temperature in the condenser

8.3.3 Pyrolysis products

The first experiences have shown that an accurate analysis of the recovered oil is not that easy due to its complex composition. For this reason, better ways and methods must be found to achieve reliable results with the available equipment. The influences of storage time and temperature as well as the different applications of the oil have to be investigated more intensively.

The hitherto neglected pyrolysis gas must be analyzed and characterized in any case to determine its potential as an energy source. The same is true for biochar (pyrolysis coke) and it´s mixture with quartz sand. It will be important for the future focus of the project to find utilization path ways for all mayor outputs products in the sense of “zero-waste” process.

9 Summary

In recent years, there has been a permanent and stable economic growth in Peru which makes it to one of the most fast growing developing countries of the world. This steady development also leads to new challenges in many areas, especially in environmental issues. Both the industrial boom and the rising life standard increase the energy consumption of the country. In order to meet this demand, renewable energy sources have to be used in the future. One very promising possibility is to meet the growing energy demand with biomass that can be found abandoned all over Peru. It can be used as a renewable and CO_2-neutral source. Moreover, biomass is the only easy available source for renewable liquid transportation fuels and chemicals. In this connection, pyrolysis can be a pre-treatment step to convert dry solid biomass into a liquid (pyrolysis oil) which has a higher energy density and is easier to handle than bulky biomass.

Pyrolysis means thermal decomposition of organic material into a range of useful products, occurring in total absence of oxygen or with a limited supply of oxidizing agents. It is always the first step in combustion and gasification processes, followed by total or partial oxidation of the intermediate products. Basically, large complex hydrocarbon molecules from the organic feedstock break down into a variety of smaller and simpler molecules of gases (like: CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc.), liquids (tars, heavier hydrocarbons, and water) and solids (mostly biochar or carbon, also called pyrolysis coke)

In order to start with pyrolysis R&D projects in Peru, a small bench scale fluidized bed pyrolysis reactor was built during this PhD-Thesis at PUCP to perform experiments on flash pyrolysis. **Flash pyrolysis** occurs in a short period of a few seconds or less in the reactor. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. In the flash pyrolysis process, biomass is decomposed to mostly vapors and aerosols and some biochar. After separating the solid products, a dark brown liquid can be recovered by cooling and condensation of the gas.

The process requires drying the feedstock to typically less than 10 wt% water content. The next step consists of grinding the feed materials in order to get sufficiently small particles (≤ 2 mm for fluid bed reactors) to ensure rapid pyrolysis reactions.

For the first experiments **ground coffee residues** were selected as feedstock in the indigenously built PUCP-pyrolysis reactor. In general, coffee is the most widely traded tropical agricultural commodity in the world, mainly used for beverages, with a production of

145 million bags per year. With the increase of the coffee production, the volume of coffee grounds as a waste is also growing. Normally, in Peru coffee grounds are disposed together with the household waste that goes mainly to landfills. In some cases, this feedstock is used as compost or deodorizer, but a major amount remains unused and can be turned into renewable energy.

The biomass “coffee grounds” for the experiments described was put into a storing tank into which nitrogen is also injected to avoid the presence of oxygen. Under the reservoir, the biomass feed quantity was controlled with a rotary feeder and the motor engine speed. A screw feeder injects the feedstock horizontally into the reactor at a height of 13 mm above the distributor plate. In the reactor, the different pyrolysis reactions are transforming the feedstock into products gas, oil and fine biochar. These products are leaving the reactor via gas flow, but it should be mentioned that some of the char particles are staying back in the reactor. Over time the reactor fills up and needs to be cleaned.

The most important **process parameters** were:

- temperature: 475 - 525 °C,
- gas flow: 10 - 15 L / min, and
- feed: 2.3 grams coffee grounds per minute.

After the reactor, a cyclone separates the solid particles before the vapor comes to a condenser. The condenser and other glass parts are made of borosilicate glass to resist the changes in temperature. With the help of a cryostat, the temperature in the condenser is cooled down to -15°C, so the oil can be separated and collected. Following the condenser an ultimate filter was installed to clean the gas before it was burned for disposal.

Oil yields up to 47 % could be achieved during these fundamental experiments with the PUCP reactor. The collected oil separates in two phases. The lighter phase is a dark liquid, much more viscous than the heavier one. Early results showed that the heavy phase contains a high amount of water. After separation, the calorific value (HHV) of the light phase could be doubled to more or less 36 MJ/kg$_{OS}$ which is nearly like domestic fuel oil (43 MJ/kg) or gasoline (41 MJ/kg). Analyses data presents also very low sulfur and inorganic mass contents.

With gas chromatography (GC-MS) it was possible to identify alkanes with 15, 17, 18, 19 and 28 carbon atoms for the light phase, and 15, 17, 18, 20, 25, 28, 31 and 33 carbon atoms for the heavy phase of the oil samples. XRF analyses indicate that main elements present in the biochar are K and Ca (> 70%) and transition metals (Fe, Ni, Cu, Mn, Zn and Ti) reach almost 25%. The semi-quantitative composition of the char-sample was determined by applying the 100 % - method. The pyrolysis gas was burned without further analysis.

By IR analysis, the presence of phenols, alcohols, alkanes and possible saturated open chain ketones, as well as aryl aldehydes were observed in the recovered oil. Another visible band in the IR could be assigned to aromatics with various types of substitution.

Peru has a great potential for the generation of renewable energy from biomass. Thus it has become a challenge to develop and offer technologies for exploiting this potential. The presented research work shows that it is possible to operate a pyrolysis reactor in Peru for the production of bio-oil. Up to now, this were only the first steps but further research work with different feedstock and larger reactors are necessary to find the most appropriate process parameters for the pyrolysis of biomass and bio-wastes available in Peru..

10 Indices

10.1 References

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10.2 Abbreviations

A	Area
BFB	Bubbling Fluidized Bed
BICGT	Biomass internal combustion gas turbine
BIGCC	Biomass internal gasification combined cycle
Bio-SG	Bio-synthetic gas
BtL	Biomss-to-liquids
°C	Grad Celsius
C_d	Discharge coefficient
c_p	Specific heat capacity [kJ/kg K]
CFB	Circulating Fluidized Bed
CHP	Combined heat and power
d_h	Grid hole diameter, [m]
DAF	Dry and Ash Free
DBFZ	Deutsches Biomasseforschungszentrum
DME	Dimethyl Ether
etc.	Et cetera (and so on)
e.g.	exempli gratia (for example)
eq.	equivalent
ESP	Electrostatic precipitator
FAME	Fatty acid methyl esthers
FAO	Food and Agriculture Organization of the United Nations
FC	Fuel cell
g	Standard gravity [9,8 m/s^2]
GWh	Gigawatt hour
GHG	Greenhouse gas
H_{mf}	Bed hight
h_{pc}	Convective heat transfer coefficient
h_r	Radiant heat transfer coefficient
h_{gc}	Gas convective heat transfer coefficient
HDO	Hydrodeoxygenation
HHV	Higher Heating Value or Gross Calorific Value
HVO	Hydrotreated vegetable oil
IEA	International Energy Agency
J	Joule
K	Kelvin [K]

LCA	Life cycle assessment or Net Calorific Value
LHV	Lower Heating Value
m_b	Mass of the particle
M	Mega
MSW	Municipal Solid Waste
N	Dumber of grid holes
N_d	Number of hole density (holes per unit area of the bed); [holes/m^2]
NGL	Natural gas liquids
No.	Number
L_B	Operating bed depth, [m]
L_h	Grid hole pitch, [cm]
OECD	Organisation for Economic Co-operation and Development
ORC	Organic rankine cycle
p.a.	Per annum; per year
Pa	Pascal [Pa]
PUCP	Pontificia Universidad Católica del Perú
Q	Gas flow rate
Q_B	Gas flow through bubble phase
Q_{mf}	Gas flow through emulsion phase when fluidization starts
R&D	Research and development
s	Second
SNV	Stichting Nederlandse Vrijwilligers; Netherlands Development Organisation
T	Tera
ΔT_{gas}	Temperature difference gas
ΔT_{ref}	Temperature difference refrigerant
t	Ton
tCO2eq	Tons of carbon dioxide equivalent
Toe	Tons of oil equivalents
U_B	Mean rise velocity of a bubble in a bed
U_{mf}	Minimum fluidization velocity
UNEP	United Nations environment program
UNFCCC	United Nations Framework Convention on Climate Change
V	Volume, [m^3]
V_b	Bed volume, [m^3]

wt%	Weight percent
ε	Voidage
ρ	Density, [kg/m^3]
ρ_b	Bulk density of fixed bed, [kg/m^3]
ρ_f	Fluid density [kg/m^3]
ρ_P	Particle density, [kg/m^3]

10.3 Tables

10.4 Figures