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Review

Thermochemical liquefaction of agricultural and forestry wastes into biofuels and chemicals from circular economy perspectives



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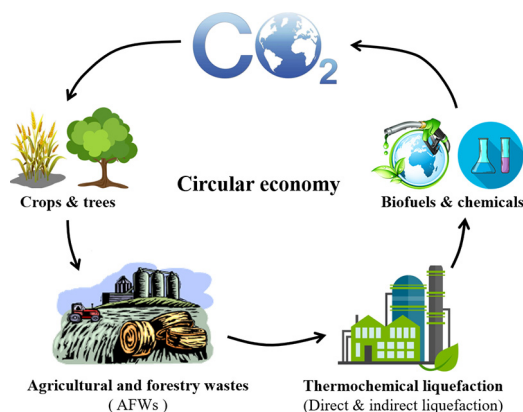
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HIGHLIGHTS

- Presenting that thermochemical liquefaction of AFWs is a promising process for producing chemicals and/or biofuels.
- This review focuses on the medium (or solvent) of thermochemical liquefaction and circular economy of product production.
- The smart use of AFWs requires a combination of available waste streams and local technical solutions to meet sustainability criteria.

GRAPHICAL ABSTRACT



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ABSTRACT

Waste produced in various fields and activities in society has been increasing, thereby causing immediate environmental harm and a serious-global problem. Recently, the attitude towards waste has changed along with innovations making waste as a new resource. Agricultural and forestry wastes (AFWs) are globally produced in huge amounts and thought to be an important resource to be used for decreasing the dependence on fossil fuels. The central issue is to take use of AFW for different types of products making it a source of energy and at the same time refining it for the production of valuable chemicals. In this review, we present an overview of the composition and pretreatment of AFWs, thermochemical liquefaction including direct liquefaction and indirect liquefaction (liquid products from syngas by gasification) for producing biofuels and/or chemicals. The following two key points were discussed in-depth: the solvent or medium of thermochemical conversion and

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Chemicals
Circular economy

circular economy of liquid products. The concept of bio-economy entails economic use of waste streams, leading to the widened assessment of biomass use for energy where sustainability is a key issue coined in the circular economy. The smart use of AFWs requires a combination of available waste streams and local technical solutions to meet sustainability criteria.

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1. Introduction

The world's population continues to grow, and the medium-variant projection indicates that the global population could grow to around 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 (DESA, 2017). Therefore, the need for new technology innovation providing a constant supply of renewable energy and chemicals has become critical for enabling sustainable development for the whole world (Sadef et al., 2016). Agricultural and forestry wastes (AFWs) are attractive feedstock for numerous biorefinery processing technologies and are the most abundant raw materials on the Earth. They are composed of carbohydrate polymers (cellulose, hemicellulose) and an aromatic polymer (lignin), which can be converted into biofuels and biochemicals by different

processes in small and large biorefineries due to its low cost, abundance and widespread availability (Millati et al., 2019; Ramarajan and Manohar, 2017). The amount of cellulose, hemicelluloses and lignin depend on the type of raw material. Usually, the cellulose content may vary between 30% and 50%, hemicelluloses 20–40% and lignin 10–30% (Fatma et al., 2018).

In the last two decades, global research programs on alternative energy have been directed towards discovering new and sustainable energy sources since the global economy can no longer depend on fossil fuels. AFWs utilized to produce biofuels have immense potential after the production cost, and market values are appropriately assessed (André Rodrigues Gurgel et al., 2019). Pretreatment is the first and most important step in lignocellulosic biomass processing. It is a key

process by which the recalcitrant lignocellulosic biomass can be modified to make it amenable to further reactions to convert it into biofuel or other products. The development of technologies on hydrothermal treatments could improve the utilization of lignocellulosic biomass through the separation of its components (cellulose, hemicellulose, lignin) in sequential processes (Eskicioglu et al., 2017; Tran, 2016a, 2016b). Low liquid to solid ratios or mild temperatures in the pretreatment step are possible ways of reducing cost. The adopted technologies for the separation and conversion of this lignocellulosic biomass into products represent an important part of the total production cost. AFWs as the feedstock are more promising than coal for thermochemical liquefaction due to its low sulfur content, nearly carbon-neutral, and obtaining valuable biofuels and/or chemicals (see Fig. 1).

AFWs are in modern society resources that can be used for producing renewable energy through the choice of suitable techniques. Biofuels for the transportation sector have been developed from different types of biomass where life cycle assessment (LCA) has been used for evaluation of carbon footprint. Sustainability issues are inherent in planning what to do with AFW, and different waste streams need to be connected in a cost-effective manner that includes ecological and societal sustainability.

Among the renewable energies, bioethanol is a typical product from the bioconversion of lignocellulosic biomass, and it widely used in some countries such as America and Brazil (Abo et al., 2019; Du et al., 2019; Mohapatra et al., 2019). Further, it has been proven to be a renewable and environmentally friendly transportation fuel. Compared with first-generation bioethanol from corn or sugarcane, the second-generation bioethanol based on lignocellulosic material has received more attention since feedstocks are nonedible food, which avoids the competition with daily food and fodder. Main factors that determine the feasibility and competitiveness of biofuels and biochemicals produced by Thermochemical conversion are the cost of biomass, yield and productivity of products, as well as separation and purification cost. This review

summarizes recent advances in the process of thermochemical conversion of agriculture and forestry wastes into biofuels and chemicals. We combine the recent technological knowledge with present environmental concerns and Bio-economy. It is not yet clear that the ways in which AFWs are used for renewable energy is entirely sustainable. The concept of Circular economy is here put forward to integrate the AFW treatment technology to sustainability in its true sense. The full-fledged Circular economy is a future ideal but now is the time to critically assess the chosen technologies for making smart use of different waste streams that at the end will be resource-efficient and having lower carbon footprint.

2. Composition and pretreatment

2.1. Composition of AFWs

Forestry waste residue comes from Woody biomass of timber logging. Food and agricultural organization (FAO) estimated that global forests cover 4 B ha (about 30% of total land area), corresponding to an average of 0.62 ha/capita (D'Annunzio et al., 2015). Of the global forest covering around 50% falls within the developing countries (Van den Born et al., 2014). The residue is stumps, branches and leaves, but then also processing waste like logs and sawdust generation. The recovery of residues depends on geographical conditions, like tree species. Estimates say that for every cubic meter of logged material that is removed from the forest, a cubic meter of waste remains in the forest. The processing waste includes branch trimming and bark removal (about 12% of this material arrives at the mill), slabs/blocks/further trimmings (about 34%) and sawdust (about 12%). Additional waste comes from kiln drying, shavings (about 6%) and sawdust/trimming (about 2%) (Thrän et al., 2017). Global wood-derived biomass production is around 4.6 Gt annually of which 60% goes to energy generation, 20% to industrial 'round wood' and the remaining 20% being primary production, which will remain in the forest to decay (Thrän et al., 2017). An estimated 80% of forest tree mass is lost as waste, with about 20% of the wood ending up in the form of kiln-dried sawn product (Tripathi et al., 2019). Based on Food and Agricultural Organization (FAO) estimations, the total AFWs and industrial wood wastes in 22 countries are depicted in Table 1. Russia, Indonesia, US, Brazil and China produce most AFWs and industrial wood wastes. From the total 715 Mt./p.a. estimation of the potential residues production could be more than 700 Mt./p.a. This loss should be turned into a resource, for example as a fuel source. In the developing countries, forestry residues remain a major energy source, as the main household fuel that significantly contributes to industrial energy consumption (Rafael et al., 2015). The composition of AFW greatly influences the performance of AFW conversion system, whether it is a liquefier or gasifier, etc. A proper understanding of the composition of AFW feedstock is essential for the design of a reliable conversion system.

Generally, the components of AFWs include cellulose, hemicelluloses, lignin, proteins, lipids, starches, simple sugars, HCs, water, ash and other compounds. The typical content (cellulose, hemicelluloses and lignin) of AFW materials is shown in Table S1. AFWs have a composite structure generally composed of 30–50% cellulose, 20–30% hemicelluloses and 5–40% lignin depending on the origin. This composition and lignocellulosic stability make a selective conversion to specific products or product classes quite difficult because different bond types (C—O, C—C and C=C, etc.) have to be cleaved and it necessitates more drastic conditions such as high temperature and pressure (Patil et al., 2014). Gasification (for the production of syngas) and liquefaction conversion are the most commonly used methods applied for converting AFW into fuels or chemicals. For example, the cereal (namely corn) can be converted to ethanol through fermentation, but the cellulosic part of the corn plant requires a more involved process through gasification or hydrolysis. The direct liquefaction of AFWs with high water content, such as rice straw, corn stalk, bagasse, willow,

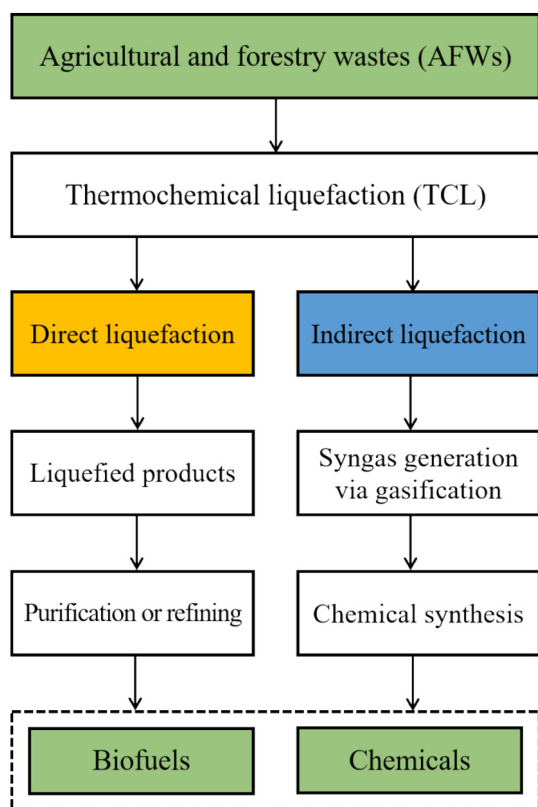


Fig. 1. The TCL routes of AFW to biofuels and chemicals.

Table 1
List of top twenty-two countries globally producing agricultural and forestry wastes (Bentsen and Felby, 2010; Tripathi et al., 2019).

Country name	Global AFWs in million tons (Mt)			Global industrial wood production wastes (Mt)			Total waste of AFWs and wood industrial waste
	Total forest waste	Total agricultural waste	Total AFWs	Waste from forest falling and cutting	Waste from wood mill	Total waste	
Russian Federation	5718	N/A	5718	68.5	27.0	95.5	5814
Indonesia	2221	N/A	2221	25.2	9.9	35.1	2256
USA	2078	682	2760	111.8	44.0	155.8	2916
Brazil	1613	451	2064	59.1	23.3	82.3	2146
China	807	716	1523	55.04	21.8	77.2	1600
Sweden	316	N/A	316	23.8	9.4	33.2	349
France	308	N/A	308	9.8	3.8	13.6	322
Finland	246	N/A	246	18.7	7.4	26.0	272
India	232	605	837	19.8	7.8	27.6	865
Philippines	162	N/A	162	1.5	0.6	2.1	164
Poland	132	N/A	132	12.5	4.9	17.4	149
Norway	81	N/A	81	3.4	1.3	4.8	86
Australia	80	N/A	80	9.2	3.6	12.8	93
Republic of Korea	65	N/A	65	1.5	0.6	2.1	67
South Africa	52	N/A	52	6.4	2.5	8.9	61
Canada	50	105	155	56.2	22.1	78.4	233
Thailand	40	N/A	40	0.01	0.0	0.01	40
UK	15	580	595	1.2	0.5	1.7	597
Japan	0	N/A	0	7.1	2.8	10.0	10
Germany	0	N/A	0	16.9	6.7	23.6	24
Austria	0	N/A	0	4.7	1.9	6.6	7
Argentina	0	148	148	N/A	N/A	N/A	148
Total	14,218	N/A	14,218	513	202	715	14,933

wood bark and sawdust, etc. (see Table S2), is a more economical process since they do not have to be dried or pre-treated.

2.2. Pretreatment of AFWs

The structure of AFWs is naturally robust as three main components of cellulose, hemicellulose and lignin are strongly bonded, which is recalcitrant to deconstruction or conversion in the biorefinery. Pretreatment is an essential component of conversion process in order to reduce the recalcitrance of AFWs, destroy the compact structure, increase biomass porosity and then promote the conversion of downstream processes. Several pretreatment methods, physical, chemical, and biological pretreatment, will be introduced in this part according to the requirement or purpose of different processes.

2.2.1. Physical pretreatment

The feed preparation means simple particle size reduction and drying that is an optional step depending on different reactor types. The size reduction methods, such as chipping, shredding, grinding, milling, can be used to enhance the digestibility of the AFWs, which increases the available specific surface area, and reduces both the degree of polymerization and cellulose crystallinity (Chen et al., 2016). HTP can be classified, according to the conditions of temperature and pressure, into steam explosion, hot-compressed water and subcritical/supercritical water treatment. Among these pretreatments, steam explosion is an environmentally friendly process because of its outstanding advantages, such as no catalyst requirement, less corrosion, and lower energy requirement (Rabemanolontsoa and Saka, 2016).

2.2.2. Chemical pretreatment

Pretreatment is required to destroy the lignocellulosic structure to make AFWs easier to convert. In chemical pretreatment with some chemicals, such as acids, alkali, organic solvents, and ionic liquids, internal lignin and hemicellulose bonds are broken, separating lignocellulosic AFWs into major fractions: cellulose, hemicellulose, and lignin (Zhang et al., 2016a, 2016b). Dilute acids, such as sulfuric, phosphoric, hydrochloric, and nitric acid, etc., can efficiently break down hemicellulose structures and release xylose. Compared with dilute acid,

concentrated acid allows high yield of sugar such as glucose, however, it is not preferred because it is corrosive to the equipment. Agricultural residues or herbaceous crops contain less lignin and are more easily disrupted at alkaline conditions (Lai et al., 2019). Alkali solutions, such as sodium hydroxide, potassium hydroxide, aqueous ammonia, etc., have a high pH, generally making lignin soluble, which forms the basis for the pulping process. Alkaline pretreatment can be conducted at lower temperature and pressure, causing less sugar degradation than acid pretreatment, but the reaction time is longer such as several hours or days (Bali et al., 2015). The use of chemicals may still be less environmentally friendly.

2.2.3. Biological pretreatment

Biological methods are environment-friendly, which can be used to reduce the polymerization of three major components of AFWs. They work in mild condition and can benefit the pretreatment stage by reducing chemical utilization and energy consumption (Lin et al., 2017a, 2017b). Biocatalysts like microbial cells or enzymes still need to be engineered and optimized in order to achieve better results (Yuan et al., 2016). Meanwhile, the high cost of biocatalyst production needs to be reduced to benefit biological pretreatment on the industrial scale. Future studies on pretreatment of AFWs should concentrate on minimizing side products and increasing the yield of main products such as glucose, xylose and lignin in an energy sufficient manner.

3. Direct liquefaction of AFW

In the past few decades, biochemical and thermochemical conversion technologies and processes have extensively been studied and applied in the preparation of biofuels and chemicals from biomass feedstock (Brethauer and Studer, 2015; Chen et al., 2015). Among these methods, a direct liquefaction process using a solvent is the most promising method for producing low molecular weight liquid fuels and/or chemicals. Liquefaction is the thermochemical conversion of wet biomass feedstock into liquid fuels and/or chemicals in a high-temperature pressurized environment (200–450 °C, 10–350 bar), which breaks down the polymer structure into liquid components (Chen et al., 2019; Huber et al., 2006). This technology is especially

suitable for the wet feedstock conversion to fuels and/or chemicals, which can be applied to a wide range of feedstocks at similar processing conditions. In recent years, the liquefaction process has widely been applied to wet biomass, such as AFWs (Yang et al., 2019).

3.1. Liquefaction processes

Carbohydrate-rich biomass of AFW is converted into chemical intermediates that can be upgraded into value-added fuels and chemicals using suitable solvents with or without a catalyst. Under thermochemical liquefaction, cellulose and hemicellulose are mainly hydrolyzed into monosaccharides and further to acids, aldehydes, ketones, etc., while lignin is degraded into phenolic compounds (see Fig. 2) (Ghosh and Haverly, 2019).

3.1.1. Cellulose

Cellulose is a polymer of glucose represented by the general formula $(C_6H_{10}O_5)_n$ ($n \approx 10,000$) and formed by the linkage of glucose through β -1,4 glycosidic bonds. These glycosidic bonds promote the formation of intramolecular and intermolecular hydrogen bonds where cellulose exists in crystalline form and does not swell in water. (Brand and Kim, 2015; Feng et al., 2018). In a gradually heated hydrothermal environment, the β -1,4 glycosidic bond in the cellulose crystal is gradually broken to form a glucose monomer. Glucose undergoes decomposition under hydrothermal conditions, and cellulose can decompose into oligomers under hydrothermal conditions, resulting in a low yield of glucose. Generally, cellulose could be converted into solubilized carbohydrates (such as glucose) by hydrothermal liquefaction, which can also be upgraded to liquid fuels, platform biochemicals, and commodity chemicals such as ethanol, liquid alkanes, 5-hydroxymethylfurfural (5-HMF), furfural, acetic

acid, etc. Kumar et al. investigated cellulose pretreatment in subcritical water at temperatures ranging from 200 to 315 °C, at 27.6 MPa, and for 3.4–6.2 s reaction times (Kumar et al., 2010). Cellulose was converted to hydrolysis products (oligomers and monomers) and a portion further degraded to the aqueous degradation products of glucose, including glycolaldehyde, fructose, anhydroglucose, and 5-HMF (see Fig. S1).

3.1.2. Hemicellulose

Hemicellulose, as the second most abundant plant material after cellulose, accounts for 20% to 30% of AFWs, is a heteropolymer composed of different monosaccharides (5-carbon sugar and 6-carbon sugar), including xylose, mannose, glucose and galactose, etc. (Lin et al., 2017a, 2017b). The composition of hemicellulose varies greatly among different biomasses: the hemicellulose of herbaceous plants mainly contains xylan, while the hemicellulose of woody plants mainly contains mannan, glucan and galactan (Feng et al., 2018). Xylan has successfully been used as a model material to study the liquefaction of hemicellulose in the presence of water or organic solvents (Wang et al., 2016). In hydrothermal liquefaction, xylan could be converted into solubilized monosaccharides such as xylose, which can also be upgraded to liquid fuels, platform compounds and valuable chemicals such as furfural, D-xylulose, glyceraldehyde, lactic acid, etc. Aida et al. studied the hydrothermal reaction of d-xylose in the water at high temperatures (350 and 400 °C) and high pressures (40–100 MPa) to elucidate the reaction pathway and reaction kinetics (Aida et al., 2010). Based on experimental results, a simplified reaction pathway (see Fig. S2) was constructed assuming d-xylulose as an intermediate for furfural and retro-aldol products by the dehydration reaction pathway, retro-aldol reaction pathway and Lobry de Bruyn-Alberta van Ekenstein (LBET) pathway.

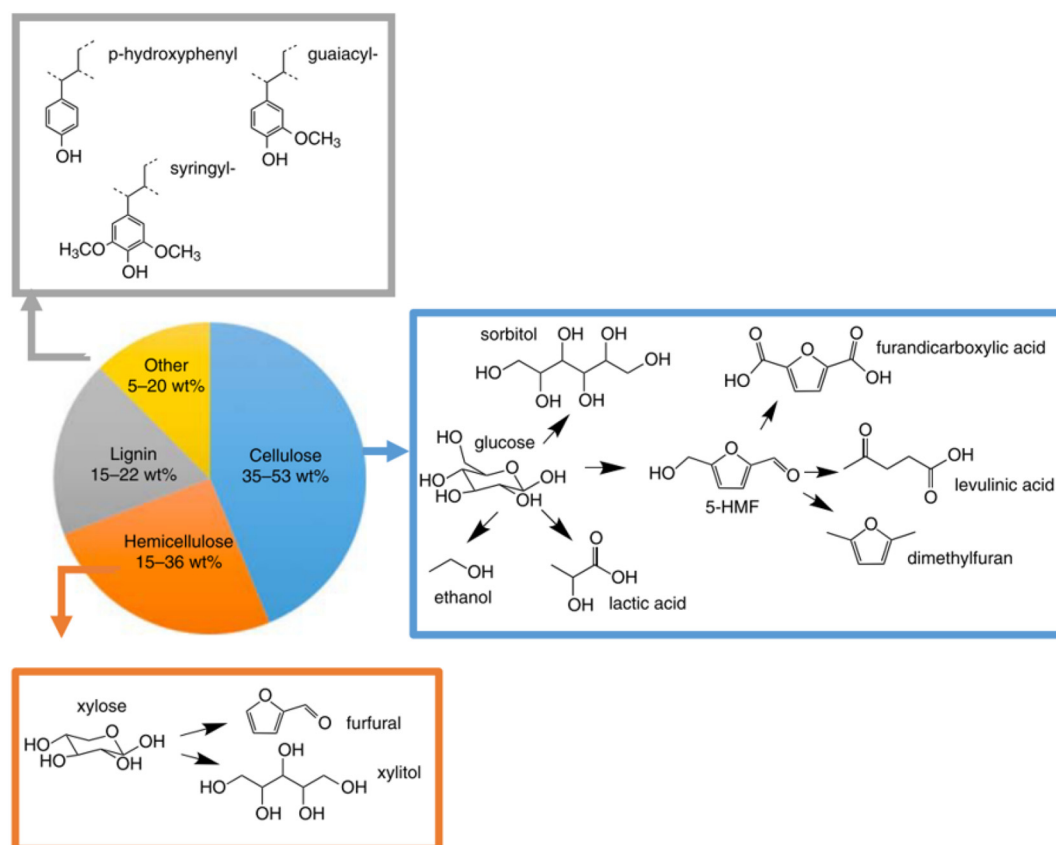


Fig. 2. Schematic of target biochemicals, and their precursors produced from biomass by solvent liquefaction (Ghosh and Haverly, 2019).

3.1.3. Lignin

Lignin is a heterogeneous aromatic biopolymer, having an approximate 10–30% dry weight and 40% of energy content in most terrestrial plants. It is one of the few renewable sources of aromatic chemicals on Earth (Sun et al., 2018). Given the structural and chemical properties of lignin itself, it contains functional groups such as hydroxyl groups and methoxy groups, which are important industrial raw materials and can replace petroleum-based chemicals as an important source of organic compounds, especially aromatic compounds (Ralph et al., 2016; Zakzeski et al., 2010). Among the lignin liquefaction methods, a direct liquefaction process using a solvent is considered to be the most promising method for producing low molecular weight liquid fuels and chemicals (Li et al., 2015; Schutyser et al., 2018). Lignin is a complex phenylpropanoid polymer held together by C—C or C—O—C bonds (Tobimatsu et al., 2012). As shown in Fig. S3, in the hydrothermal liquefaction of lignin for phenolic production, hydrolysis and cleavage of the C—O—C and C—C bonds, demethoxylation, alkylation and condensation reactions take place and main reactions are competitive (Kang et al., 2013).

3.2. Liquefaction technologies

In the process of direct liquefaction, the solvent has a significant effect on the AFWs. The interaction between the solvent molecule and the biomass molecule directly affects the distribution and composition of the liquefied product (Motagamwala et al., 2016). Generally, the solvent in AFW liquefaction has many functions: dissolving and dispersing the raw material, stabilizing the reaction intermediate or inhibiting its repolymerization, and additionally providing the hydrogen source to improve the quality of the liquefied products (Kruse and Dahmen, 2015). At present, direct liquefaction of AFW in the presence of a single-phase such as water, organic solvent, mixed solvent or supercritical fluid, have extensively been studied (Shuai and Luterbacher, 2016). There are especially many potential green solvent options for biomass feedstock processing in future (see Fig. 3).

3.2.1. Liquefaction in water

Water is one of the most studied solvents, which is environmentally friendly and inexpensive. In addition, water plays an active role in the liquefaction processes as solvent, reactant and catalyst or catalyst precursor. Water properties, such as density, dielectric constant and ionic product, etc., have a significant effect in the range of temperatures from 200 °C to 450 °C (Fig. S4 a). The properties of water change around the critical temperature need to be sufficient to facilitate liquefaction: the dielectric constant drops by about 80% to allow improved solubility of non-polar compounds, but the ionic product is still high enough (above $\sim 10^{-14}$) to favor ionic reactions. These reactions will then result in oil products (Fig. S4 b) rather than radical reactions resulting in solids (coke) or gases (Castello et al., 2018). Temperatures beyond and above

the critical temperature are referred to as the hydrothermal carbonization and gasification regime, respectively (Fig. S4 b). The AFW itself contains water, and these feedstocks can be converted directly without drying if they contain 60% or more water (Olmstead et al., 2013). Hydrothermal conversion of the AFW processes provides the opportunity to use feedstocks for the formation of energy carriers or platform chemicals. Based on these advantages, a large number of studies have been carried out using aqueous solvents for AFW liquefaction (Nazari et al., 2015; Tran, 2016a, 2016b), achieving good results (as summarized entry 1–8 of Table 2).

3.2.2. Liquefaction in organic solvent

Water is the most widely used AFW liquefaction solvent, which is cheap and environmental benign. When water is used as a liquefaction solvent for AFWs, there are also many problems: 1) The critical point of water (374.3 °C and 22.1 MPa) is high, which gives higher requirements for instruments and equipment, harsh operating conditions and increased costs. 2) The yield of insoluble products such as aromatic compounds and bio-oil is low in a water solvent. 3) The liquid product has a high oxygen content (30–50%) and a low calorific value (Gunawan et al., 2013; Verma et al., 2018). Therefore, to improve the yield and calorific value of chemicals and bio-oil products, more and more researchers are using organic solvents such as small-molecule alcohols and ketones instead of aqueous solvents for research (see entry 9–12 of Table 2). Organic solvents such as methanol (239.5 °C, 8.1 MPa) and ethanol (240.8 °C, 6.1 MPa), whose critical points (and boiling point, dielectric constant, etc.) are much lower than that of water, could succeed in the liquefaction of AFWs into valuable bio-oils and chemicals under mild reaction conditions.

Organic solvents can be classified into three categories according to their polarity: polar protic, dipolar aprotic and non-polar solvents (Reichardt and Welton, 2014; Shuai and Luterbacher, 2016). The polar protic solvent refers to a solvent in which a hydrogen atom is bonded to an electronegative atom, such as a small molecule alcohol solvent. Dipolar aprotic solvent is a solvent, which does not contain O—H and forms double or multiple bonds between C and O or N atoms, such as acetone and tetrahydrofuran. Non-polar solvents are compounds having a low dielectric constant and being immiscible with water, such as benzene, diethyl ether, and dichloroethane. Table S3 lists the types and examples of organic solvents for the AFW liquefaction.

Liquefaction of AFWs with proper solvents is a process that can prospectively be integrated with optimized conditions to produce fuel additives and valuable chemicals, simultaneously (Liu and Zhang, 2008). Compared with the water solvent, the critical temperature and pressure of the organic solvent are both low. From the viewpoint of the liquefaction reaction, the reaction conditions using the organic solvent are milder, and the requirements on the instruments and equipment are also relatively low. When the organic solvent is used for AFW liquefaction, its reaction effect is remarkable, and it has great potential in the field of AFW liquefaction for bio-oil and chemicals production (Isa et al., 2018). The use of the organic solvent could also yield some problems, for example, a high cost of the solvent should be considered; the application and recycling of a large quantity of organic solvent (such as methanol and phenol) result in environmental concerns (Kang et al., 2013). Fig. S5 shows the advantages and disadvantages of water and organic solvents as liquefaction solvent (Huang and Yuan, 2015).

3.2.3. Liquefaction in complex solvents

Based on the above discussions, the use of water or organic solvents as liquefaction solvent has its own advantages and disadvantages. In view of this, the liquefaction in mixed solvents of water-organic solvent is proposed to combine the advantages of water and organic solvents (Zhang et al., 2019). The organic solvent/water mixed solvent refers to a system in which the organic solvent is miscible or miscible with water. The mixed solvent can not only dissolve AFWs well, but also have a good solubility to the reaction product, so that AFWs can have

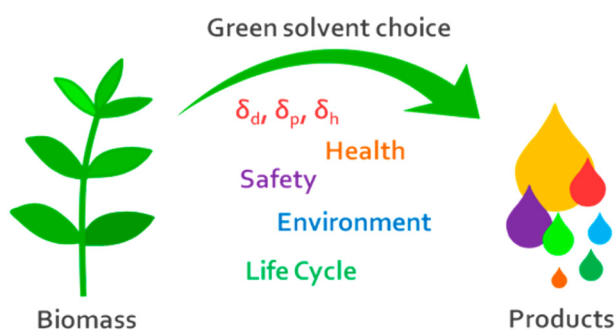


Fig. 3. Green solvents in biomass processing (Soh and Eckelman, 2016).

Table 2
Summary of recent research progress in hydrothermal liquefaction (HTL) of AFWs in different solvents.

Entry	Feedstock	Liquefaction conditions					Products	Reference
		Temperature [°C]	Pressure [bar]	RT ^a [min]	catalyst	solvent		
1	Brown macro-algae ^b	350	–	15	–	Water	Bio-crude yields between 9.8 wt% and 17.8 wt% (daf) with HHVs between 32 and 34 MJ/kg and bio-char yields between 10.9 wt% and 18.6 wt% (db) with HHVs between 15.7 and 26.2 MJ/kg	(Anastasakis and Ross, 2015)
2	Rice straw	300	120	30	–	Water	Recovery of sugar, aromatics and acetic acid from hydrolysates of rice straw.	(Lyu et al., 2015)
3	Rice straw	280–320	60–90	–	–	Water	HTL of rice straw under N ₂ showed high conversion (78%) and bio-oil yield (17 wt%) compared to O ₂ and CO ₂ . The major compounds were composed of phenol, guaiacol, syringol and their derivatives.	(Singh et al., 2015)
4	Oil palm residues ^c	330–390	250–350	30–240	–	Water	Optimum bio-oil yield of 38.5 wt% is obtained at 390 °C and 25 MPa for 60 min	(Chan et al., 2015)
5	Beech wood	300	10	60	–	Water	High iodine value (126 g I ₂ /100 g of fuel) bio-oil is obtained	(Haarlemmer et al., 2016)
6	Birch wood saw dust	300	90	30	KOH	Water	The bio-oil yield with KOH was around 40 wt% (un-catalyzed experiment, ~18 wt%). The products were mainly phenol derivatives 7(2-methoxy-phenol) and aliphatic compounds.	(Nazari et al., 2015)
7	<i>Litsea cubeba</i> seed	250–350	30–120	60	Na ₂ CO ₃	Water	The highest bio-oil yield of 56.9 wt% was achieved at 290 °C, 60 min. The higher heating values of the bio-oil were estimated at around 40.8 MJ/kg.	(Wang et al., 2013)
8	Waste plastics	400	250	15	–	Water	Plastics convert into their monomers and value-added chemical compounds. Nearly 100% conversion of PC (Polycarbonate) into synthetic crude oil.	(Helmer Pedersen and Conti, 2017)
9	Kenaf ^d and wheat straw	250–350	50	60	Ru/C	Tetralin	Higher oil yield of hydrolysates was 77.2% at 300 °C for kenaf.	(Meryemoğlu et al., 2014)
10	Barley straw	280–400	–	15	K ₂ CO ₃	Acetone	Bio-crude yield was enhanced gradually with aqueous phase addition at 300 °C, and reached 38.4 wt% after three cycles.	(Zhu et al., 2015)
11	Rice straw	270–345	–	15–30	–	Ethanol	Bio-oil yield of 47.8 wt% was obtained at conditions of 320 °C, 15 min.	(Yang et al., 2018)
12	Cellulose	250–375	–	15	H ₂ SO ₄	1,4-Dioxane	A maximum levoglucosan yield of 51% was achieved at 350 °C using 0.25 mM sulfuric acid in pure 1,4-dioxane.	(Ghosh and Brown, 2019)
13	Lignocellulose biomass ^e	300	–	15	–	Ethanol-water	The liquefaction efficiency in three reaction media with respect to the bi-crude yield followed the order of water/ethanol mixed solvent > pure water > pure ethanol regardless of the feedstocks.	(Feng et al., 2018)
14	Mulberry bark	300	–	60	K ₂ CO ₃	Ethanol-water (E-W)	The liquefaction efficiency was higher in E-W (95.7 wt%) than that in water (87.5 wt%). And the yield of light oil was low (4.16% in E-W and 2.56% in water).	(Chen et al., 2018)
15	Cornstalk	250–320	–	30	–	Methanol-water	Methanol and water exhibited a synergic effect on the cornstalk liquefaction. The yield of bio-oil reached 52.4% at 300 °C for 30 min.	(Zhu et al., 2014)
16	Kraft lignin	290	20 ^f	120	HTaMoO ₆ and Rh/C	1,4-Dioxane-water	The Rh-HTaMoO ₆ was found to be the best to convert the lignin to liquid fuel, giving liquid product yield of 95.6% at 290 °C for 2 h and BO-2 yield of 58.7% at 320 °C for 24 h.	(Jin et al., 2018)
17	Cornstalk powders	300–350	20	120	K ₂ CO ₃	Phenol-water	Cornstalk were effectively liquefied in a hot-compressed phenol-water medium (1:4 wt./wt.). The optimum temperature was around 350 °C, where the liquid yield attained a maximum at about 70 wt%.	(Wang et al., 2009)
18	Rice straw	260–350	60–180	3	–	2-Propanol-water	The maximum yield of bio-oil was 39.7% for the 2-propanol: water volume ratio of 5:5 at 573 K, while the HHV of bio-oil increased with the reaction temperature and solvent volume ratio.	(Yuan et al., 2007)
19	Kraft lignin	225–325	–	30–180	–	Ethanol/1,4-dioxane/ formic acid	A combination of ethanol, 1,4-dioxane and formic acid (10:10:2, v/v) was selected as liquefaction solvent for Kraft lignin, resulting in a low residue yield of 6.57% and a high phenolic monomer yield of 22.4% at 300 °C for 2 h.	(Wu et al., 2019)

^a RT, residence time.

^b Four brown macro-algae: *L. digitata*, *L. hyperborea*, *L. saccharina* and *A. esculenta*.

^c Oil palm residues: Raw empty fruit bunch, palm mesocarp fiber and palm kernel shell.

^d Kenaf, *Hibiscus cannabinus* L.

^e Lignocellulose biomass, organosolv lignin, cellulose.

^f The initial hydrogen pressure was 20 bar.

a good contact with the catalyst and greatly improve the reaction efficiency. In addition, low-molecular alcohols such as ethanol undergo a “reforming” reaction together with water in the hydrothermal process, generating hydrogen in situ as a hydrogen supplier, which is advantageous for reducing the oxygen content in the liquefied product (Isa

et al., 2018). Mixed solvents thus have potential advantages and have received extensive attention and research in recent years.

The organic solvent (such as ethanol, methanol, phenol, etc.)-water mixed solvents have been applied to the liquefaction of various AFWs, such as cornstalk, rice straw, barks, wheat straw, sawdust, etc. as

shown in Table 2 (see Entry 14–19). Research shows that the use of organic solvent water mixed solvents could further enhance the AFW liquefaction, resulting in higher conversion rate and bio-oil yields. Among all the organic solvent–water mixed solvents tested, alcohol–water mixed solvents have more commonly been employed. In a previous work of Yan et al., poplar liquefaction (PL) in methanol, water, or water/methanol cosolvents was investigated at 240–320 °C for 0–90 min. They found that the yields of bio-oils obtained from PL in water/methanol are higher than those in either methanol or water, indicating that methanol has a synergic effect with water on PL (Yan et al., 2015). Patil et al. studied hydrothermal liquefaction of wheat straw into bio-oil under subcritical conditions in water and water–alcohol mixtures. The water–ethanol mixture was found to be a very reactive medium showing a complete biomass conversion and > 30 wt% yield of high caloric oil (Patil et al., 2014). Fang et al. further reported that the water/ethanol mixture was extremely efficient for lignocellulose liquefaction. The oil yield followed the order of water/ethanol mixed solvent > > pure water > pure ethanol regardless of the feedstocks (Feng et al., 2018).

3.3. Liquefaction products

Direct liquefaction is a complex combination of various AFWs and processes to produce value-added products such as fuels and/or chemicals. It is necessary to consider suitable solvents, energy consumption, and carbon footprint information, etc. before choosing feedstocks and processes in designing an optimum system (Ragauskas et al., 2014). When targeting chemicals, a key objective is to maximize the product selectivity to favor the subsequent separation. For the production of fuels, attention should be paid to the establishment of an energy-efficient process for high-quality fuels. This can be realized through the design of C–C coupling reactions and the development of multifunctional catalysts to minimize reaction steps from lignocellulose to fuels (Jing et al., 2019). The product portfolio of the liquefaction processes in terms of solid, liquid, and gas products is shown in Fig. 4 (Cao et al., 2017).

3.3.1. Biofuel definitions

The term biofuels are used in several ways and primarily it means fuel that originates from living organisms in the biosphere like plants but also microscopic organisms like algae. Sometimes the word is used already to denote biomass and often the refined biological material that is working directly as fuel. The diversity of meanings is also reflected in the division of biofuels into first, second, and third generation biofuels (Correa et al., 2017). The first-generation biofuel originates from agricultural crops like corn, sugarcane, sugar-beet, soybean oil and palm oil. The second-generation comes from agricultural waste like fruit waste, cooking oil and industrial waste. The third-generation biofuel is produced from Algae feedstock (Centore et al., 2014). The fourth-generation is photobiological solar and

electro fuels that originates from algae and cyanobacteria. Agriculture and forestry generate substantial amounts of wastes resulting from harvestable yield. It is estimated the waste biomass is roughly 140 Gt 1,2 causing large problems with management in the form of undesirable environmental impacts.

3.3.2. Biofuels for transportation

Direct liquefaction of whole AFWs typically results in a wide range of products. Among these products, biofuels have an energy content of 70–95% of that of petroleum fuel oil (Cao et al., 2016; Jindal and Jha, 2016). Liquid biofuels can generally be categorized as alcohols, drop-in biofuels and/or fuel additives. Methanol, a C₁ alcohol, is traditionally synthesized from syngas (CO and H₂) derived from the gaseous products removing CO₂. Drop-in biofuels that are pure hydrocarbons are fully compatible with existing fuel utilization systems (Zhang, 2016). AFWs can be processed into fuel additives to improve engine performance. Examples include methanol, ethanol, butanol, dimethyl ether (DME), and oxymethylene ethers (OME) (Zhang et al., 2016a, 2016b). Transportation fuels derived from the AFWs are shown in Fig. 5.

3.3.3. Chemicals for revenue

Although biofuels are produced in much larger volumes from AFWs, commodity chemicals potentially represent much larger revenue from AFWs. In recent years, the production of a wide range of chemicals from biomass has been demonstrated (Brethauer and Studer, 2015; Zhang, 2016). Carbohydrate-rich biomass such as AFW is converted into chemical intermediates that can be upgraded into value-added chemicals or fuels using suitable solvents with or without the catalyst. Cellulose or hemicellulose feedstock such as herbaceous could be used for producing solubilized carbohydrates at high yield and selectivity by solvent liquefaction method. These solubilized carbohydrates can be upgraded to platform biochemicals and/or valuable chemicals such as ethanol, liquid alkanes, 2-dimethylfuran, 5-hydroxymethylfurfural, furfural, acetic acid, etc. (Cao et al., 2015; Luterbacher et al., 2014). Another kind of valuable chemicals such as aromatic compounds from lignin feedstock via solvent liquefaction is aromatic fuel, chemicals, or their precursors. Lignin-rich materials such as soft and hardwood from AFWs can be used for the production of a variety of aromatic monomers such as guaiacol, 2,6-dimethoxyphenol, coniferyl alcohol, and the γ -methyl ethers as guaiacyl or syringyl lignin-derived products (Minami and Saka, 2003).

4. Indirect liquefaction of AFWs

Gasification is a process in which agricultural and forest industry wastes, such as crop straw, forestry scrap, or sawdust, react with air, oxygen, and/or steam to produce a gas product called syngas or producer gas that contains CO, H₂, CO₂, CH₄, and N₂ in various proportions (Huber

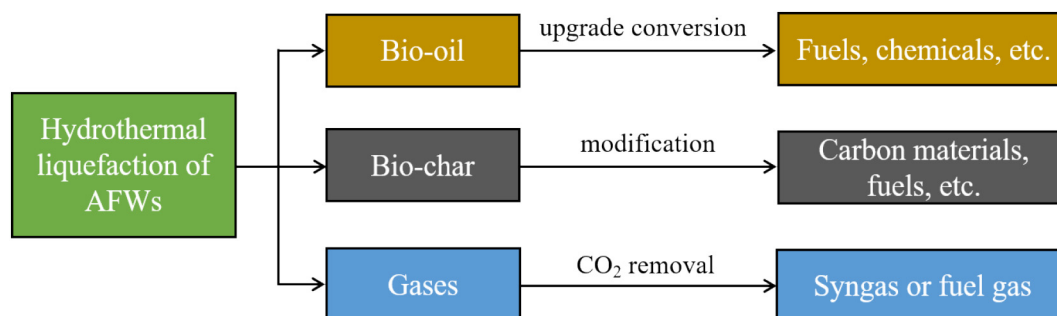


Fig. 4. Products from hydrothermal liquefaction of AFWs (Cao et al., 2017).

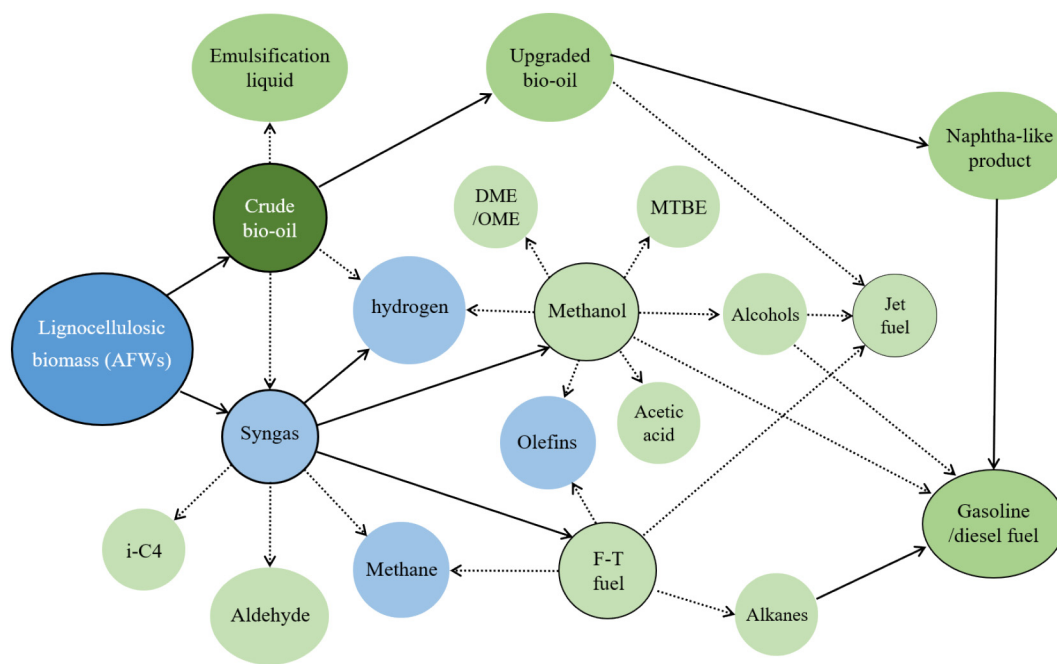
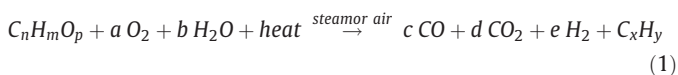


Fig. 5. Network of bio-fuels and allied fuel additives from Lignocellulosic biomass (AFWs). F-T: Fischer-Tropsch; i-C4: isobutene and isobutane; MTBE: Methyl tert-butyl ether; HRJs: hydro-processed renewable jet fuels (Zhang, 2016).

et al., 2006). Gasification of AFWs is an efficient and environmentally friendly way to produce biofuels and/or chemicals, which is similar to coal gasification with a few differences. As the AFWs are more reactive than coal, gasification of AFWs occurs at a lower temperature (400–1000 °C) than coal gasification (Olgun et al., 2011). The resulting gaseous product called producer gas is an energy-rich mixture of combustible H₂ and CO gas, which is the basis of the syngas (Beyene et al., 2018). The synthesis gas can then be converted into liquid fuels and chemicals by two different commercial processes: Fischer-Tropsch synthesis (Ellis et al., 2019; Gruber et al., 2019) or methanol/dimethyl ether synthesis (Dalena et al., 2018; Vita et al., 2018). Gasification, i.e. indirect liquefaction, thus shows great promise because it can reduce environmental pollution, guarantees the energy security, and encourages economic development.

4.1. Gasifying processes

AFW gasification occurs through a sequence of complex thermochemical reactions and hence, it is unrealistic to split the gasifier into different zones carrying out many gasification reactions simultaneously. These complex reactions involved in gasification process are shown in Fig. S6. A combination of reactions in the solid, liquid, and gas phases occur during the gasification including oxidation, drying, pyrolysis and reduction (Molino et al., 2016). Exothermic combustion reactions provide the heat required for the gasification process or it is thermally provided from external sources. When the gasification reaction doesn't produce tar, charcoal or black carbon, the composition of gaseous products can simply be expressed by the following eq. (1) (Isha and Williams, 2011; Sikarwar et al., 2016):



The major reactions occurring during gasification are depicted in Table 3 (Molino et al., 2018; Sansaniwal et al., 2017; Sikarwar et al., 2016):

4.1.1. Drying

Various physical and chemical characteristics of raw AFW material play a vital role in the gasification process. Generally, two types of moisture content are taken into consideration in the AFW feedstock, namely the intrinsic moisture, which is the water content of the material without taking the impact of weather into account; and the extrinsic moisture, which incorporates the influence of weather conditions (Sikarwar et al., 2016). Depending on the nature of AFW, the moisture content generally varies from 5% to 35%, which is converted into steam at a temperature of around 100 °C. This makes them more suitable for thermal conversion since most gasifiers are designed to accommodate the feedstock. A lot of AFWs possess a higher amount of moisture, which causes energy loss and degrades the quality of the product. Usually, drying is done prior to gasification to counter this problem. The moisture contents of some AFW are shown in Table S2

Table 3
Fundamental Reactions and chemical reaction energy of gasification process.

Classification	Elementary reaction	Chemical reaction heat (ΔH, kJ/mol)
Drying	Moist feedstock → feedstock + H ₂ O	(2) –
Pyrolysis	Feedstock → char + volatiles ^a	(3) –
	C + O ₂ → CO ₂	(4) –394.0
	C + 1/2 O ₂ → CO	(5) –111.0
Oxidation	H ₂ + 1/2 O ₂ → H ₂ O	(6) –242.0
	CO + 1/2 O ₂ → CO ₂	(7) –284.0
	CH ₄ + 2O ₂ → 2CO ₂ + 2H ₂ O	(8) –803.0
	C + CO ₂ → 2CO ^b	(9) 172.6
	C + H ₂ O → CO + H ₂ ^c	(10) 131.4
Reduction	CO + H ₂ O → CO ₂ + H ₂ ^d	(11) –42.3
	C + 2H ₂ → CH ₄ ^e	(12) –75.0
	CH ₄ + H ₂ O → CO + 3H ₂ ^f	(13) 206.3
Tar cracking	Tar + H ₂ O → CO + H ₂ + CO ₂ + C _x H _y ^g	(14) –

^a CO, CO₂, H₂, CH₄, H₂O (g).

^b Boudouard reaction.

^c Reforming of char.

^d Water gas shift (WGS) reaction.

^e Methanation reaction.

^f Steam reforming of methane.

^g Steam reforming of tar.

(Biagini et al., 2015; Han et al., 2017; Li et al., 2018; Sikarwar et al., 2016; Szamosi et al., 2017; Zeng et al., 2017).

It's clear from Table S2 that rice husk, wheat straw, rape straw, switchgrass, miscanthus and pine sawdust are preferred over rice straw, corn stalks, bagasse, willow, wood bark, poplar and sawdust for gasification, based on low moisture content, which is one important factor for selection of the gasifier. The low moisture content is favorable since it has a lower energy penalty in the drying process prior to gasification.

4.1.2. Pyrolysis

The pyrolysis reactions take place with temperatures in the range of 200–700 °C (Molino et al., 2016; Sfakiotakis and Vamvuka, 2018). They are endothermic and, as in the drying step, the heat required comes from the oxidation stage of the process. At low temperatures, the kinetics of the reactions may be the limiting step, while at higher temperatures the heat transfer or the product diffusion may become the limiting step. During pyrolysis, both the process of drying and reduction of molecular weight takes place simultaneously, while the moisture gets removed below 200 °C. When the temperature increases to 300 °C, the reduction of the molecular weight of the AFW constituent's mainly amorphous cellulose starts with the formation of carbonyl and carboxyl group radicals. When the temperature exceeds 300 °C, the resultant crystalline cellulose is decomposed with the formation of char, tar, and gaseous products. The hemicellulose is decomposed into the soluble polymer with the formation of volatile gases, char, and tar. The lignin gets decomposed at a higher temperature varying from 300 to 500 °C forming methanol, acetic acid, water, and acetone (Sansaniwal et al., 2017). In short, the large main biopolymers such as, cellulose, hemicellulose, and lignin get converted into the carbon and medium-size molecules (CO, CO₂, H₂, CH₄, etc.) and the pyrolysis process is shown in the reaction (3) of Table 3 and Fig. 6 (Basu, 2013a).

4.1.3. Oxidation

Most gasification reactions are generally endothermic. To provide the required heat for the reaction, drying, and pyrolysis, a certain amount of exothermic combustion reaction is allowed in a gasifier. During the oxidation process, the volatile materials from the AFW get oxidized under exothermic chemical reactions and generate the heat with peak temperature varying from 1100 to 1500 °C with gaseous fuels like CO, H₂, CO₂ and H₂O (Sansaniwal et al., 2017). Oxidation

reactions are generally faster than gasification reactions under similar conditions. Table S4 compares the rate of oxidation and gasification for a biomass char at a typical gasifier temperature of 900 °C (Reed, 2002). The oxidation rates are at least one order of magnitude faster than the gasification reaction rate. Owing to pore diffusion resistance, finer char particles' oxidation (or combustion) has a much higher reaction rate. The main reactions that take place during the oxidation phase can be schematized with the reactions (4)–(8) in Table 3.

4.1.4. Reduction

The reduction step involves the products of the preceding stages of pyrolysis and oxidation, where the gas mixture and the char react with each other resulting in the formation of the final syngas. The main chemical reactions occurring in the reduction step are listed in Table 3 (reactions 9–13). The gasification process not only produces the useful gas but also some undesirable by-products (such as NO_x, SO₂, tar, etc.). The biggest obstacle in the utilization of the producer gas is too much tar, which will reduce the AFW utilization efficiency. The temperature at which the reduction step is carried out has a fundamental role in determining the composition of the syngas and characteristics of the solid residue (such as tar). The influences of temperature are depicted graphically in Fig. S7 (Molino et al., 2016). The formation of tar particles can be controlled by setting up adequate temperature conditions ensuring thermal decomposition in the reduction zone. High temperatures increase the oxidation of solid residue and reduce the formation of tar (Fig. S7). A temperature of 1000 °C in the reduction zone has been reported suitable for the requisite reduction of tar particles (Valderrama Rios et al., 2018).

4.2. Gasifying technologies

Gasifying medium (also called “agent”) plays a vital role in the gasification process, which reacts with solid carbon and heavier hydrocarbons to convert them into low-molecular-weight gases like CO and H₂. The main gasifying agents used for gasification are air, steam, and oxygen. The choice of gasifying agent affects the heating value of the product gas as well. Table S5 summarizes the heating values of three gasification agents (Basu, 2013b; Parthasarathy and Narayanan, 2014; Saxena et al., 2008). Oxygen gasification has a higher heating value compared to air and steam gasification (Table S5). Air results in the

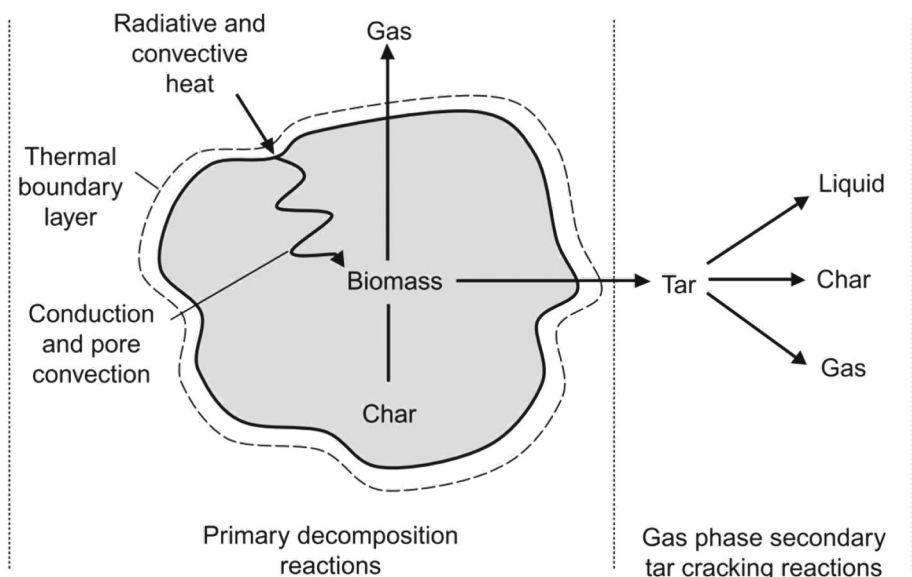


Fig. 6. Pyrolysis process in biomass material (Basu, 2013a).

lowest heating value in the product gas primarily due to the dilution effect of nitrogen.

4.2.1. Gasifying in air

Air is the most common agent for gasification because it is abundant in nature and inexpensive to employ. The performance of air gasification heavily depends on the equivalence ratio (ER), which is the ratio of the actual air-fuel ratio to the stoichiometric air-fuel ratio. For the quality of gas obtained from a gasifier, the value of ER must be significantly below 1.0 to ensure that the fuel is gasified rather than combusted. In practical scenarios, the ER's value is normally maintained within the range of 0.20–0.30. Basu et al. studied that the variation in carbon conversion efficiency of a circulating fluidized-bed (CFB) gasifier for wood dust against the ER (Basu, 2013c). Higher ER (>0.4) results in lower H₂ and CO yields, with an increase in CO₂ amount, which causes a decrease in the heating value of the gas. Conversely, an excessively low ER value (<0.2) results in several problems, including incomplete gasification, excessive char formation, and a low heating value of the product gas (Hamad et al., 2016; Wang et al., 2015). Liu et al. (2018) demonstrated the results of gasification change according to a variation of equivalence ratio (ER) from 0.15 to 0.24 with airflow rate 0.6 Nm³/h during gasification at 700 °C. With the rising ER, an increasing degree of combustion reactions releases heat to intensify tar secondary cracking reaction. Adding air as gasification agent can promote oxidation reaction from CO and O₂ to CO₂ and promote complete oxidation reaction of fixed carbon and O₂, thus the CO₂ rises and the CO drops.

4.2.2. Gasifying with steam

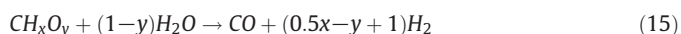
Superheated steam is used as a gasification medium either alone, with air, or with oxygen. It contributes to the generation of hydrogen (see Reaction 10 in Table 3) with a higher heating value compared to air and oxygen gasification. The ratio of steam-to-biomass (S/B) is an influential parameter that affects the input energy requirements, outlet gas quality and product yields (Parthasarathy and Narayanan, 2014). Low S/B ratios result in higher amounts of char and CH₄ whereas increasing S/B positively enhances the reforming reactions by providing an oxidative environment, thereby raising the oxidized product gas yield. Hernández et al. discovered that as the S/B increased, the H₂ and CO₂ content in the gas increased while the CO and CH₄ decreased. Steam also reduces the content of recalcitrant by-products during the gasification process (Hernández et al., 2012). Kihedu et al. compared air and air-stream gasification of biomass pellets in a packed bed reactor, where air gasification resulted in a tar content of 75.3 g/m³ of gas while that of air-stream gasification produced a lower tar content of 58.7 g/m³ of gas (Kihedu et al., 2016).

4.2.3. Gasifying with oxygen

Oxygen employed as a gasification agent is used primarily to provide the thermal energy needed for the endothermic gasification reactions. The bulk of this heat is generated through the partial and/or complete oxidation reactions of carbon (see Reaction 4 and 5 in Table 3). If oxygen is used as the gasifying agent, the products include CO for a low amount of oxygen and CO₂ for high oxygen. The equilibrium calculations show that as the oxygen-to-carbon (O/C) ratio in the feed increases, CH₄, CO, and hydrogen in the product decreases but CO₂ and H₂O in the product increases. Hamad et al. (2016) explored the equivalence ratio (ER) for the gasification of cotton stalks by changing the weight of biomass while keeping the amount of oxygen constant. The effect of ER on the gasification process was studied by varying the ratio in the range of 0.12–0.4. In this range, minimum char production was achieved for an ER of 0.4 while the gas yield was the highest. Table S6 shows that increasing ER means a lower heating value of produced gas and lower hydrogen content. An ER of 0.25 was determined to be the best ratio for gasification under the investigated experimental conditions, which gives more gas and higher hydrogen yield.

4.3. Products from syngas

The AFW which is low in ash content is generally employed for syngas production, because high ash content causes slagging, such as rice husk. Syngas is one of the key products of AFW gasification and is a blend of CO and H₂ (as depicted in Reaction 15), which is a vital source of environmentally benign fuels and chemicals (Huber and Corma, 2007; Wilhelm et al., 2001). For many years, biomass-derived syngas has been used as a raw material in different thermochemical processes for the production of second-generation biofuels (Demirbas, 2011), both liquids, (such as methanol, ethanol, dimethylether (DME), and Fischer-Tropsch diesel) and gaseous (such as hydrogen and synthetic natural gas (SNG)) (Yan et al., 2010). Spath and Dayton (Molino et al., 2018; Spath and Dayton, 2003) carried out a techno-economic screening for the production of fuels and chemicals from biomass-derived syngas, identifying several syngas conversion routes to methanol and its derivatives, such as DEM, ethanol, Fischer-Tropsch (FT) synthesis, hydrogen, and SNG. These products can be divided into two broad groups: (1) transportation fuels (e.g., hydrogen, biogas and biodiesel), and (2) chemical feedstock (e.g., methanol, ammonia and dimethylether).



4.3.1. Hydrogen as transportation fuel

Transport fuel and a large number of chemicals are produced from different syntheses of CO and H₂ (Brown, 2019). Currently, the predominant share of hydrogen is produced from steam reforming of hydrocarbons such as natural gas, coal and oil. Only 5% of hydrogen is produced from other renewable sources such as biomass (Parthasarathy and Narayanan, 2014; Sinigaglia et al., 2017). As fossil fuels are declining and the Greenhouse effect is causing problems, it is high time to look for an alternative source of hydrogen generation in the near future. During the gasifying agents, pure steam gasification (see Reaction 15 in Section 4.3) produces higher H₂/CO and hydrogen yield (Yao et al., 2016). Hydrogen-rich gas can be produced from AFW gasification using steam as a gasifying agent. After the transformation of biomass into syngas, the gas mixture is further treated in the same way as the product gas of the pyrolysis process, as shown in Fig. 7.

At present, H₂ is considered a valuable and clean alternative to fossil fuel that feeds low-temperature fuel cells, such as proton exchange membrane (PEM), and allows electric energy conversion, avoiding pollutant and greenhouse gas emissions (Nikolaidis and Poullikkas, 2017). AFWs are renewable energy sources that can be used to produce hydrogen sustainably. Hydrogen recovery from AFWs is sufficient to satisfy the present and future hydrogen demands (Dou et al., 2019). A lot of technologies exist for transforming the energy-rich biomass into hydrogen. Summary of hydrogen generation from various AFWs sources are given in Table 4.

4.3.2. Liquid hydrocarbons by Fisher-Tropsch synthesis

Syngas can directly be transformed to liquid hydrocarbons such as diesel and kerosene fuels and/or gases via a number of distinct processes, such as Fischer-Tropsch Synthesis (FTS) (Lappas and Heracleous, 2016). The interest in FTS increased owing to its importance in the production of oil from biomass (Kreutz et al., 2008). The FT process can produce hydrocarbons of different lengths from syngas originating from any carbon-containing feedstock, such as AFWs. The composition of biodiesel, gasoline and biogas may not be exactly the same as in petroleum, but they perform the same task with near zero carbon emission, which is one of the most promising routes for the production of sustainable fuels. The production of synthetic biofuels comprises three basic steps in all FT processes: gasification of the feedstock (AFWs) for production of synthesis gas (CO and H₂) and gas cleaning/conditioning, FTS for middle distillates production, and

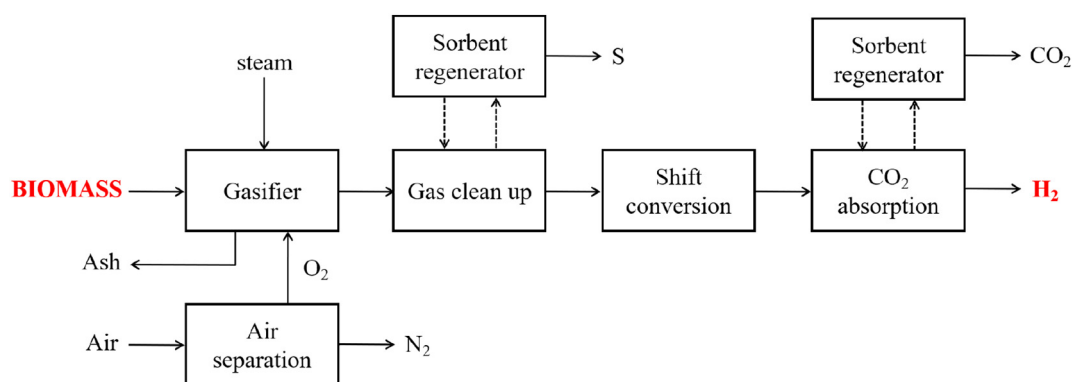
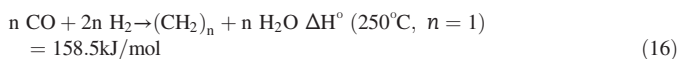


Fig. 7. Flow diagram of the biomass gasification process (Nikolaidis and Poullikkas, 2017).

upgrading of the FT liquids to high-quality fuel products (Kim et al., 2016; Luque et al., 2012). These three main sections are illustrated in Fig. 8.

FTS reaction produces a range of hydrocarbon for use as transport fuel like gasoline, diesel, and as chemical feedstock. They include some desirable products like olefins, paraffins, and alcohols, and some undesirable products like methane, aldehyde, acids, ketone, and carbon, etc. Generally, the Fischer-Tropsch process as represented by the reaction 16 (Ail and Dasappa, 2016), is operated in the temperature range of 150–300 °C to avoid high methane byproduct formation (see the reaction 17) and the pressure range of one to several tens of atmospheres to favor formation of desired long-chain alkanes (see the reaction 18, 19 and 20).



where “(CH₂)_n” represents a product consisting mainly of paraffinic hydrocarbons of variable chain length.



The catalysts play a pivotal role in the FTS process. Many studies found that Group VIII metals have highest catalytic activity in FTS reaction. The FT reaction is catalyzed mainly by Fe, Co, Ni and Ru catalysts

(Gavrilović et al., 2018; Luque et al., 2012), which possess sufficiently high hydrogenation activity for use in the synthesis process. Currently, there are two operating modes for the FT reactors: high temperature mode (300–350 °C) and low temperature mode (200–240 °C). Most common reactors include fixed-bed reactor, bubbling fluidized bed reactor, slurry-bed reactor, and circulating fluidized-bed reactor (Klerk and Furimsky, 2011).

Many studies have considered production of FT liquid transportation fuels (such as biodiesel) from a variety of AFW sources, especially when used in combination with solar or wind energy (Samavati et al., 2018). Müller, et al. investigated the integration of hydrogen from wind power promoting a combined power-to-gas and biomass-to-liquid process (Müller et al., 2018). The results showed that an increased gas stream feed, enabled by the addition of hydrogen from wind power, leads to an increased output of Fischer-Tropsch products (diesel and kerosene). Gruber et al. presented a new insight, “Wind diesel” technology, which enabled the integrative use of excess electricity combined with biomass-based fuel production (Gruber et al., 2019). The experiments showed that integrating renewable H₂ into a biomass (wood chips-to-liquid), the Fischer-Tropsch concept could increase the productivity while product distribution remains almost the same. In the solid FT fraction, a n-paraffin of up to 82.2 wt% was determined, whereas in the liquid fraction the maximal reported n-paraffin was 77.7 wt%.

4.3.3. Chemical feedstock

Syngas is used not only as an energy source but also as a feedstock for the production of “green chemicals.” Commercially it finds use in two major areas: (1) alcohols (e.g., methanol and higher alcohols) and (2) chemicals (e.g., glycerol, fumaric acid, and dimethylether). When syngas from AFW gasification is used for chemical production, the cleaning of the raw gas is needed strictly in order to remove contaminants and potential catalyst poisons (such as particulate matter, alkaline

Table 4
Summary of several representative studies of hydrogen production from AFW gasification.

Feedstock	Gasifying medium	Conditions	Products	Reference
Pine sawdust	Air-steam	700–900 °C in a fluidized bed	H ₂ (20–40%), CO, CO ₂ , CH ₄ and C ₂ H ₄	(Lv et al., 2004)
Pine sawdust ^a	Steam	600–850 °C in a fluidized bed	H ₂ (30–52%), CO, CO ₂ , CH ₄ and C ₂ H ₄	(Yan et al., 2010)
Wood pellets	Air-steam	Max. temp. of 950–1150 °C in a fixed bed gasifier	H ₂ (25–35%), CO, CO ₂ , CH ₄	(Plis and Wilk, 2011)
Woody biomass and agriculture residue ^b	Steam-oxygen	Circulating fluidized bed gasifier	H ₂ (20–25%), CO, CO ₂	(Meng et al., 2011)
Pine and spruce wood	Steam/CO ₂ ^c	1000–1400 °C in a solar reactor	H ₂ (35–40%), CO, CO ₂ , CH ₄	(Bellouard et al., 2017)
Waste biomass ^d	Supercritical water	Tubular batch reactor, NiCe/Al ₂ O ₃	H ₂ (30–40%), CO ₂ , CH ₄ , C ₂ -C ₄	(Kang et al., 2016)
Wheat straw	Steam	A two-stage fixed bed, Ni/AC catalyst	H ₂ (35–75%), CO, CO ₂ and CH ₄	(Yao et al., 2016)
Wood residue	Air-steam	A research scale fluidized bed, Ni/CeO ₂ /Al ₂ O ₃	H ₂ (24–42%), CO, CO ₂ , CH ₄ , C ₂ H ₄	(Peng et al., 2017)

^a The actual feedstock was biomass char, which was produced by fast pyrolysis liquefaction of pine sawdust in a fixed-bed reactor.

^b Agro, willow, and DDGS (dry distiller’s grains with soluble).

^c Solar gasification.

^d Canola meal, wheat straw and timothy grass.

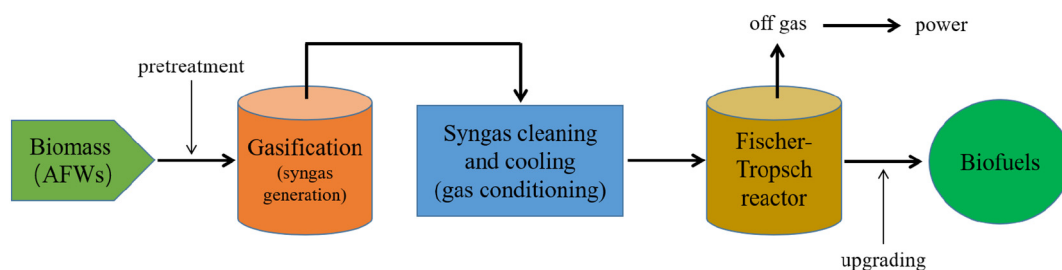


Fig. 8. Schematic line-up of the biofuel production from AFWs via gasification and FTS (Kim et al., 2016; Luque et al., 2012).

metals, sulfides, nitrides and halides, etc.) (Woolcock and Brown, 2013) as well as to achieve the qualitative composition required by the chemical production process. In order to enhance the chemical production process, the production of syngas has to be carried out in operative conditions required for its end use as much as possible, especially the steam-reforming step and the WGS reaction. The following section briefly describes the production of some of these products.



Methanol is produced through the synthesis of syngas (CO and H₂) in the presence of catalysts (see Reaction 21), which is an important feedstock for the production of several chemicals such as olefins as well as for fuels such as gasoline over zeolite catalysts (Venkik and Yang, 2017). Methanol synthesis is an exothermic reaction influenced by both temperature and pressure. As a result, the yield of methanol increases with pressure (in the 50–300 atm range) but decreases with temperature (in the 240–400 °C range). In the absence of a suitable catalyst, the actual yield is very low, and catalysts are used based on Zn, Cu, Al, and Pd (Behrens et al., 2012). The dominating catalyst is Cu-based, promoted with Zn(O), containing a typical support material such as alumina in industrial production (Li et al., 2019). This catalyst has high selectivity to methanol and exhibits a cost advantage compared to the other materials active in this reaction: e.g. Pd, Pt. There are some possible disadvantages, such as the tendency towards sintering at temperatures greater than 270–300 °C. It is a reaction mechanism that requires carbon dioxide to be present in the feed, resulting in water as a by-product in the reaction (Porosoff et al., 2016). Considering the above questions, many researchers have shown that doping or using noble metal catalysts can improve the sintering and methanol selectivity. Supported palladium has been suggested as an alternative catalyst because the reaction mechanism proceeds via carbon monoxide and it is possibly a more active metal than copper. Pd based catalysts may be an alternative to Cu-based catalyst as they possess better tolerance towards Sulfur poisoning, which is becoming increasingly important for coal or biomass derived synthesis gas feed (Phan et al., 2016). Both Pd/CeO₂ catalysts show high initial activity in the stacked foil micro structured reactor (SFMR) and fixed-bed reactor (FBR), respectively, but deactivate significantly to reach steady state after 60–120 h on the stream.



5. Biofuel and chemical production in circular economy

Waste has in Europe become a resource in a short period of time after the idea of Circular economy (CE) was spreading through the

continent. The trade and business sector estimates that circular economy-type economic transitions may add up to 600 billion euros annual economic gains for the EU manufacturing sector (Beaulieu et al., 2016; COM, 2015; EMAF, 2015). China has been in the forefront promoting the idea of CE already several years ago by being the first country in the world, to even adopt a law about the circular economy in 2008 (Beaulieu et al., 2016). CE is associated with a variety of concepts, and waste management emerges as the most relevant sub-sector.

AFW treatment deals with material and energy flow in the society. When looking at the traditional material and energy flow it is typically linear that has been described as extract-produce-use-dump material model visioned by Frosch and Gallopoulo (1989). That way of handling material use is not sustainable. Activities abiding this model has instigated a lot of damage in the world where urbanization has been and still is the dominating societal trend causing ecological shortcomings affecting human life and the environment where we live. The circular economy provides a different model for material and energy flow that is circular, which should and could be the basic principle in biofuel production.

5.1. Linear or circular model of economy

What is then wrong with the typically linear model? The model can be described by the ‘parent system’ with the economic system being part of that. The parent system has also physical dimensions and the size of different ecosystems has been shrinking exemplified by deforestation and growing desert areas. The parent system used to be more constant but now its quality is continuously threatened and is not able to produce traditional ecosystem services as in the past (Korhonen et al., 2018). The climate change is leading to rise in sea level and reduced spaces of habitable land in the pacific area. The economic system is growing and spreading, but is in conflict with the parent system causing clashes like the reduction of the Amazon rain forest in Brazil at the moment where the Brazilian state wants to capitalize the rich natural resources in the region to boost biofuel production to improve the national economy (Ferrante and Fearnside, 2020). In this linear model, wastes are just dumped back to nature causing pollution and lowering of the quality of the parent system with global consequences in change of weather conditions to more extreme events of draught or heavy rain-falls causing floods and landslides in other parts of the world. The economic system is competing with the parent system tearing it down by not recognizing ecological facts governing the life on earth.

The solution to combatting this harmful development in linear material and energy flow is to adopt the opposite circular model, which would mean careful use of resources aiming at zero waste (Geissdoerfer et al., 2018). Once the raw material has been extracted and manufactured to a product, it makes economic sense to keep its value in circulation as long as possible. The thought is to use and recycle materials in as high value products as possible and keep it in active use as long as possible. It is fundamental to retain the high value of the product/material/service (Ludekefreund et al., 2019). That will demand that they from the beginning are designed to be used for multiple lifecycles and at the end the products will return (with appropriate business model) and they will be remanufactured for use in the next lifecycles.

5.2. The path of economy to sustainability

The multiple life cycles encompass the return of materials/energy to nature. Materials like bioenergy, pulp, paper and timber, can be part of nature economy-nature-economy etc. cycles. Wastes should and are part of joint renewable cycles. In the economic realm of cradle-to-cradle business there are “biological nutrients” contained by industries where biomass is released back to biosphere contributing to biomass growth and biodiversity which supports nature and in turn will support the resource basis of economics in nature (Korhonen et al., 2018).

The challenges for implementing CE are great because approximately 75% of the energy production is currently based on non-renewable sources taken from the lithosphere, which are combusted. This leads to emissions to biosphere overloading the natural system. This situation shows very barely, where we are now and that there is a long way globally to go to reach the current CE visions (Korhonen et al., 2018). The increased growth of biomass may help society to substitute non-renewable and emission intensive fossil fuels but unfortunately, a lot of nutrient rich biomass is combusted for energy. A CE type of solution is to utilize the resources nutrient value better, like in deliberate nutrient cycles to produce food. The point here is that nutrients are used before combustion, so that these nutrients are not lost. Here is the great opportunity for CE to use existing nutrient cycles in nature.

Korhonen et al. put forward ideas that apply to modern CE systems to extend current business or corporate environmental management systems encouraging inter-sectoral, inter-organizational and inter-life cycle material cycles and energy cascades (Korhonen et al., 2004, 2018). The goal is to receive the highest economic resources value. In this vision CE is inter-organizational and network environmental sustainability management (Seuring and Gold, 2013). To reach towards this goal much work is needed since Interorganizational systems seem to be self-organized (Chertow and Ehrenfeld, 2012) making the planning, design and management more difficult.

5.3. Planetary boundaries and limitation of natural resources

The most debated planetary boundary of the nine depicted is Climate change. The Intergovernmental Panel on Climate Change (IPCC) formulated a “climate goal” of 2 °C not be exceeded in order to avoid disastrous global effects (Pachauri and Reisinger, 2014). As the warming is induced by CO₂ emissions –it would require that cumulative CO₂ emissions from all anthropogenic sources should remain below some 3650 Gt CO₂ (1000 GtC), but over half this amount has already been emitted by 2011. The use of bio-based resources instead of fossil ones would be a high priority GHG mitigation option.

The planetary boundaries concept presents a set of nine planetary boundaries within which humanity can continue to develop and thrive for generations to come (<http://www.stockholmresilience.org/research/planetary-boundaries.html>) (Steffen et al., 2015).

1. Stratospheric ozone depletion.
2. Loss of biosphere integrity (biodiversity loss and extinctions).
3. Chemical pollution and the release of novel entities.
4. Climate change.
5. Ocean acidification.
6. Freshwater consumption and the global hydrological cycle.
7. Land system change.
8. Nitrogen and phosphorus flows to the biosphere and oceans.
9. Atmospheric aerosol loading.

The UN has put forward them as defining the resonant capacity of the Earth and the describing the vulnerability of our natural resources (Steffen et al., 2015). Both the processes of climate change and land system change are already beyond the safe operating zone. The biosphere integrity, such as genetic diversity, and biogeochemical flows (nitrogen

and phosphorus flow to the biosphere and oceans as a consequence of industrial and agricultural processes) related to agricultural waste are at high risk.

6. Conclusions and outlook

In recent decades, there has been an increasing effort to reduce the reliance on fossil sources and regulate the greenhouse gas emission. The use of biomass wastes as raw material is becoming a major alternative to fossil fuels or chemicals, since it is widely abundant and relatively inexpensive. AFWs are considered promising alternatives to supply biofuels and/or chemicals by thermochemical liquefaction. Although many lab-scale investigations have been carried out on the thermochemical conversion, commercial production and utilization of biofuels and/or chemicals are still at an early stage. In this review, we have discussed several important factors including AFW pretreatment, reaction medium (or solvent), catalyst development, process optimization, separation of oil and gas, which still need to be systematically performed at bench, pilot scale and even industrial level.

Various pretreatment strategies may give preferred results relying on specific project goals and the choice of feedstock. Because of different properties of AFWs, woody biomass, e.g. poplar or eucalyptus, is more resistant to breakdown than herbaceous biomass such as switchgrass. Many potential green solvent (or medium) options currently already exist, which proves applicability to AFW processing. The availability of these solvents, particularly for neoteric solvents, are necessary for their future development. The choice of solvents (or medium) used for AFW processing will in part determine both the economic viability and environmental sustainability of the thermochemical liquefaction. Eventually, the cost of thermochemical conversion should be reasonable and acceptable.

Biofuel and/or chemical production is technically possible from different types of AFW, that vary with climatic regions in the world. The continuous and stable availability of the biomass is important to ensure upscaling of the refinery process. A great challenge is in different countries to acknowledge pinpoint the different waste streams and start to combine them for production of valuable products in a profitable manner. This endeavor requires multidisciplinary and better communication between different organizations and government bodies. An essential prerequisite is that the growing of the biomass should not compete with food production at agricultural land, but straw residues from crops are of course usable biomass. To ensure sustainability criteria in the process, environmental certification has become an important tool for improving the image of the biofuel product on the market. Overall, the profitability of advanced technologies for AFW treatment has to be studied in a higher degree and the focus in future should be in combining ecological aspects with economic and societal sustainability.

Declaration of competing interest

Authors have no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.141972>.

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