Recent developments in key bio-refinery areas

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**Abstract**

In order to meet decarbonisation goals and implement a more sustainable circular economy model, the chemical industry needs to transition from fossil to renewable sources of carbon. Current chemical production is dominated by petroleum where this broadly uniform feedstock is separated using a single, simple process to give a small range of heteroatom free molecules that are the platform to a myriad of products. In a bio-refinery however, many feedstocks of widely varying composition using markedly different technologies are processed to give one or two of a wide range of bio-derived platform molecules. Here recent publications are used to highlight selection of the most suitable second or third generation feedstocks converted using integrated, complementary processes in order to generate multiple products. This approach generates a range of chemicals, more fully utilising the carbon source of choice in a sustainable manner, generating more value, which together makes the realisation of the bio-refinery concept draw ever closer.

**Introduction**

One of the greatest challenges that humanity faces in the 21st century is developing a more sustainable society for future generations[1]. The decrease in primary resources, coupled with ever-increasing volumes of waste are two of the most significant factors that pose a major threat to achieving this sustainability. The uncontrollable growth of these factors does not come as a surprise, given that most of the 20th century followed the linear economic model of ‘take-make-consume-throw away’, fuelled by a swiftly growing industry that led to a huge spike in consumer demand[1-3]. This rapid growth in industry came as a result of the presence of cheap, readily available and abundant mineral resources.

The problem with this linear economic model is that it caused an irreversible autocatalytic process; whereby an increase in consumer demand led to an increase in industrial production which resulted in a reduction in costs and hence a lower perceived value of products by consumers.[4] Once the value of a product is lowered, its usefulness is short-lived and the desire to dispose of it greatly increases – leading to the widely adopted ‘replacement before redundancy’. Therefore, sustainability can never be achieved if this model continues to be followed since: (i) traditional, fossil-based resources are becoming ever-more scarce and expensive, especially since most of the readily-accessible fossil-based resources have already been extracted, leading to the need for much more energy-intensive and expensive processes to obtain them. (ii) The disposal of huge volumes of articles has led to a large accumulation of waste in landfill sites as well as uncontrolled release into the environment, the worryingly vast quantities of plastics accumulated in the seas and oceans being a prime example of this[1, 4].

Change therefore needs to occur, both by the consumer (in terms of attitudes towards the value of products) and, more importantly, by industry. Even today, the generation of chemicals and energy is still reliant on fossil-based resources in industrialised countries. It is essential that this concept of linear economic model is replaced with the circular economy model, *i.e.* material flows in the whole economic system in a closed loop[2]. In this model, materials (resources and products) are utilised for as long a time as possible while products are recovered at their end-of-life and incorporated back into the system (either whole or as individual resources) to maximise their use and lower waste. In order for this to be achieved, there must be a transition from the fossil-based economic production system, which follows the linear economic system towards the so-called bio-economy[4]. Bio-economies aim to provide energy and products based, at least partly, on renewable feedstocks. This involves the production of readily-recyclable, bio-degradable products using clean, environmentally-friendly production technologies[5]. The latter description encompasses the ‘biorefinery concept’. In order for biorefineries to slowly start displacing crude petrochemical refineries (and move towards a bioeconomy), there has to be a way for biorefineries to generate the same valuable products provided by the petrochemical refineries, both in terms of quality and cost; some of which include agrochemicals, pharmaceuticals and nutraceuticals, textiles, plastics, pigments and dyes, personal care products, home products *etc.*[4, 5]

This mini-review aims to give an updated critical overview on the biorefinery concept, highlighting key research that has been conducted in the past two years with respect to feedstock selection, green processing technologies and future outlook.

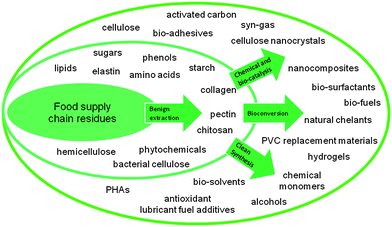
**Feedstock: Selection is key**

When going down the biorefinery route, one of the first and most crucial factors to consider is the choice of renewable feedstock – this is a critical step, as being ‘renewable’ does not necessarily equate to being green and environmentally sustainable – a clear example of this is the early adoption of palm oil in the production of biodiesel; the introduction of vast areas of commercial palm plantations in Southeast Asia has led to the irreversible destruction of natural ecosystems through deforestation, peatland destruction and animal extinction[6]. There is also the ever-growing concern about ‘food vs non-food’. From this aspect, it would be vital to focus on the use of ‘non-food’ biomass, with bio-waste (biomass waste) being the prime candidate. Bio-waste can include a host of different waste streams including agricultural residues, food waste, municipal solid waste and sewage sludge. However, it is important to note that the organic composition constituting these waste streams may not be 100% bio-based, such as the ever-increasing presence of non-renewable plastic polymers in agricultural and municipal solid waste. Below we have highlighted the key feedstocks that have been investigated in the past few years for biorefinery applications.

**Lignocellulosic Feedstock**: The most abundant bio-derived feedstock on the planet is lignocellulosic biomass, with an annual production in excess of 185.1 billion tonnes[7] , with a significant proportion already available as waste/by-products of established industries. This makes it the most obvious start point for replacing the vast sums of materials produced *via* the petrochemical industry and encompasses all plant material from woodland, to agricultural residues to grasses and garden waste. The exact composition of lignocellulosic material varies from species to species, although in all cases it is dominated by cellulose which is an insoluble polymer consisting of 1-4 linked C6 glucopyranose units. This in turn is coated by hemicellulose, a mix of C6 and C5 units, the exact nature of which vary, *e.g.* in softwood this is predominantly D-mannose and D-glucose, while in hardwood it is xylose alongside α-arabinofuranose and α-glucuronic acid. Both cellulose and hemicellulose have been used as feedstocks in both chemo and bio-catalytic process to give small compounds and/or free sugars in high yield and selectivity. The third major constituent is lignin, usually forming within the biomass once growth is complete, giving structural reinforcement as well as making the plant less susceptible to environmental stresses. Lignin is the most abundant natural source of aromatic compounds, being comprised of coniferyl, sinapyl and p-coumaryl alcohols and as such is an area of great interest. However due to its function within the plant, lignin is incredibly incalcitrant and has proved a difficult feedstock towards efficient production of small compounds. Finally, all freshly harvested lignocellulosic feedstocks also contain extractives although these can vary wildly in yield, functionality, composition and potential value.

**Microalgae** - The use of microalgae for the generation of chemicals and energy has attracted much attention in recent years as a result of their exceptional advantages when compared to terrestrial lignocellulosic plants; namely: (i) significantly higher photosynthetic efficiency (5 – 20%) leading to higher production/growth rates (ii) the ability of production throughout the year. The main focus of microalgae, currently, is utilising its lipophilic fraction for biodiesel production; however, this fraction only constitutes approximately 10% of the total weight of the biomass and there is, therefore, a huge proportion that is underutilised[8, 9]. These underutilised proportions comprise mainly of pigments, carbohydrates and proteins, with the latter being of particular interest due to the presence of biologically-fixed nitrogen, which would enable the generation of high-value nitrogen-containing compounds that are important platform molecules in the pharmaceutical, chemical and textile industries as well as for CO2-fixation. Current production of nitrogen containing compounds involves the use of petrochemical resources in highly complex processes that are massively energy intensive[8].

**Food Waste**: Currently, one of the largest accumulations of bio-wastes around the world is food waste (FW), whereby around 1.3 billion tones y-1 of food is wasted according to reports from the United Nations Food and Agriculture Organisation (FAO)[10, 11]. This waste accumulates over the entire ‘food life cycle’, *i.e.* from the primary production (generation of waste from agricultural residues) through to the secondary production (waste generated from industrial processing) and finally waste associated with human consumption[11, 12]. This food waste is normally divided into avoidable and unavoidable food waste; while the former can be reduced by taking certain precautionary measures at each stage of the life cycle, the latter requires more innovative approaches to address the issue *via* reuse and recycling strategies[12]. One area that has been highly investigated using FW is biogas generation *via* anaerobic fermentation while other areas that have been explored include the generation of biohydrogen, biomethane, liquid biofuels, electricity and commodity chemicals[11, 13-16]. Figure 1 summarizes potential bio-products obtained from food waste and their applications in consumer products[17].



**Figure 1. Potential applications of bioproducts obtained from food waste in consumer products. *Reprint with permission from [17]* Lin CSK, Pfaltzgraff LA, Herrero-Davila L, Mubofu EB, Abderrahim S, Clark JH, et al. Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. Energy Environ Sci. 2013;6:426-64. Copyright RSC 2013.**

**Municipal Solid Waste (MSW):** MSW is solid waste that constitutes a variety of components including plastics, glass, metals, food, textiles *etc.* The actual composition of MSW varies from place to place (cities and countries) depending on a number of factors including cultural practices, legislation, waste management and economic factors *e.g.* in Asia and North Africa, MSW is dominated by organic waste (*ca.* 61-62%)[18]. It has been estimated that approximately 1.3 billion t y-1 of MSW is generated, and this is expected to increase by almost two-fold (2.2 billion t y-1) by 2025[19]. MSW often ends up in landfills (around 90% in developing countries) and is considered to be a serious environmental problem, as its decomposition contributes significantly to greenhouse gas emissions, along with other factors including heavy metal poisoning[18]. Currently, the major waste management strategies (from a biorefinery perspective) for dealing with MSW has been its incineration for energy recovery and the generation of syngas *via* MSW gasification for electricity generation,[20] although this represents a loss of useful functionality.

**Green Technologies**

Although there are significant quantities of biomass available in order to provide chemicals and energy, thus far heat and power generation has been the dominant application for biomass processing at full commercial scale[21]. Provision of chemicals, fuel and energy from biomass has encountered numerous issues at both pilot and commercial scale, as a result of the complexity and variation in the physical and chemical compositions of different biomass – which leads to (i) highly complex process operations (ii) high costs associated with processing (iii) low conversion of biomass to products. There has been extensive research worldwide to develop novel, efficient methods to process biomass, within a biorefinery context, in order to address these challenges[21, 22].

**Extraction:**  Extraction of surface and free molecules is a step that is often omitted from biorefinery concepts, with destructive technologies often directly employed; in fact, on large commercial scales, extraction technologies are typically utilised as standalone technologies. Introducing a non-destructive extraction technique as a first step in a biorefinery would be beneficial as it will further improve biomass valorisation by providing added-value and high-value chemicals including essential oils, waxes, steroids, flavonoids and other phenolic compounds, carotenoids and other pigments, high MW lipids[23]. These chemicals have a wide range of applications and are utilised in nutraceutical, pharmaceutical, household, cosmetic and food industries[23, 24].

Conventional batch solvent extraction using an organic solvent has remained the dominant type of extraction, however, there have emerged a number of alternative, cleaner candidates including supercritical/subcritical extraction, ultrasound extraction, microwave-assisted extraction and a combination of these extraction technologies (e.g. microwave-assisted/ ultrasound-assisted extraction) which may better fit into a biorefinery set-up[25]. Of these, supercritical CO2 (scCO2) extraction especially shows significant promise, as besides being a non-destructive technology, it leaves no solvent residues, which means that the post-extracted biomass can be directly passed onto the next stage of the biorefinery process without any time-consuming, energy intensive drying/solvent removal procedures if necessary[23]. This is shown in Figure 2 below. However, since scCO2 extraction is an expensive technology, it should provide products that are considered to be ‘high-value’ in order to be economically viable. A good example of this is a recent study conducted by Attard *et al.* that looked at valorising hemp waste *via* scCO2 extraction[26]. The hemp residue waste in question was ‘hemp dust’ that is generated in the processing of hemp fibres, is considered to be of ‘zero-value’ and was utilised solely for production of energy. Carrying out scCO2 extraction, prior to a destructive technology, on this dust at 350 bar, 50 oC (optimised conditions) gave rise to extracts containing considerable quantities of cannabidiol (CBD). This is very interesting, as it is often assumed that CBD is restricted to the top of the plants. CBD is a high-value molecule, costly and in extremely high demand due to its plethora of therapeutic properties. Therefore, scCO2 extraction on this waste residue could be a promising first step in a biorefinery set-up providing a high-value product, which could then be processed further using more destructive technologies to provide other chemicals and energy[26].



**Figure 2. Incorporation of supercritical extraction as a first step in an integrated biorefinery. *Reprint with permission from [23]*** Attard TM, Bukhanko N, Eriksson D, Arshadi M, Geladi P, Bergsten U, et al. Supercritical extraction of waxes and lipids from biomass: A valuable first step towards an integrated biorefinery. J Clean Prod. 2018;177:684-98***.* Copyright Elsevier 2018).**

**Hydrothermal pretreatment:** A common technique employed in biorefinery applications is hydrothermal pretreatment which, essentially, refers to heating plant material with water or steam at elevated temperatures to disrupt and depolymerise the lignocellulosic structure, making cellulose and hemicellulose more easily accessible to enzymatic degradation; depending on the pressure and temperature employed, hydrothermal pretreatment can be generally divided into: (i) subcritical water ( 100 – 374 oC) (ii) supercritical water (>374 oC)[27].

Various types of residues, originating from the agricultural and food industries, have been investigated for obtaining fermentable sugars using hydrothermal pretreatment. When considering hydrothermal pretreatment, it is important to factor in that the technological treatment of each biomass varies significantly, with different combination of parameters, as a result of the large variations in biomass composition. Typically, there are three general modes in which hydrothermal pretreatment is carried out: batch, semi-continuous and continuous[28]. The first two are often employed to study the parameters affecting hydrolysis (raw material, temperature x time (severity), pressure, catalyst, flow rate, solvent-to-feed ratio), however, they have limited application at commercial level due to complex automation problems. Continuous mode shows more promise for scale up due to significantly shortened hydrolysis times, selectivity of products and reduced equipment size, however, energy efficiency of the process remains a problem[28, 29].

Hydrothermal pretreatment of residues from the coffee industry has received much attention of late[30, 31]. Subcritical water hydrolysis of coffee powder and defatted cake was conducted in semi-continuous mode; for the coffee powder, conditions of 300 bar and 150 oC resulted in 9% total reducing sugars while for the defatted coffee cake, 17.2% total reducing sugars was achieved with conditions of 225 bar and 175 oC[30]. In a more recent study, subcritical water was employed in a semi-continuous reactor to treat spent coffee grounds at varying temperatures, pressures and flow rates. The two major products obtained were oligosaccharides and phenolic compounds, with yields of 33.7 g/100 g-1 and 4 g/100 g-1 spent coffee grounds respectively using conditions of 200 oC, 70 bar and 10 ml min-1[31]. Semi-continuous subcritical water hydrolysis has also recently been employed to spent brewer’s grain and rice straw[32, 33]. In the former study, selective production of C5 sugars from hemicellulose (90% hydrolysed) was achieved, with the major compound being arabinose followed by xylose. Sugar yields correlated strongly to the solvent-to-feed ratio and hydrolysis temperature, with the best yields obtained at 210 °C, 20 mL and solvent-to-feed ratio of 64[32]. In the latter study, the cellulose and hemicellulose from rice straw were hydrolysed to reducing sugars (70 wt%), whereby 33.4 wt% fermentable sugars and 0.77 wt% levulinic acid were achieved at 250 bar and 220 oC[33]. A similar study was also conducted on rice husks by the same authors[34].

Coupling hydrothermal pretreatment with other pretreatment technologies can lead to fractionation of high-value products. In a recent study by Toscan *et al.*, hydrothermal pretreatment was coupled with imidazole delignification of elephant grass in a two-stage process[35]. The hydrothermal pretreatment was conducted at 180 oC resulting in a liquor that was dominated by gluco- and xylooligosaccharides and pentose sugars. The remaining solid residue was recovered and pretreated with imidazole at 140 oC for approximately 3 h, leading to high delignification (83.8 wt%) and significant enrichment of cellulose (97.7 wt%). This pretreatment stage subsequently led to high enzymatic hydrolysis yields of glucan to glucose[35].

**Thermochemical treatment**: Thermochemical treatment refers to heating procedures that lead to a decomposition of the biomass residues producing both chemicals and fuels[36]. Traditionally, the main thermochemical treatment applied to biomass has been combustion, which is thermal degradation in the presence of oxygen. The aim of this procedure is for heat generation or obtaining electricity with a generator. Recent interest in the potential production of fuels and chemicals from biomass has led to the application of other thermochemical routes which can be summarized into as follows:

**Pyrolysis**: a thermal degradation of organic compounds in the absence of oxygen or air to produce various gaseous components as well as bio-oil and char residues[37].

**Liquefaction**: thermal treatment of biomass generally applied in the presence of a solvent to break down the biopolymeric structure primarily into liquid components[37].

**Gasification**: heating up a solid or liquid carbonaceous material with some gasifying agent to produce gaseous fuels (often called syngas fuel)[37].

The challenge with thermochemical treatments is the need for an effective separation method of the obtained product mixture. When lignocellulosic material is treated via pyrolysis, three different and useful fractions are obtained: a gaseous fraction (also called syngas) that typically consists of H2, CO, and CO2; condensable gases (loosely termed “bio-oil”) that are complex mixtures of organic compounds; and a solid fraction called char whose calorific value is generally higher than that of the original biomass[38]. These three materials are quite useful given that they can all be burnt to generate energy, they can be converted into biofuels, materials or for the generation of chemical products. Furthermore, bio-oil and syngas are of particular interest as they can also provide platform molecules, such as guaiacols, furfurals and levoglucosenone to name but a few, that have the potential to replace petroleum-derived chemicals[38]. Lately, a remarkable number of studies have applied microwave technology to the pyrolysis of biomass in an attempt to make the process greener as discussed below.

Microwave assisted pyrolysis (MAP) relies on the ability of the material to absorb microwaves. The dielectric constant of corn stover, for example, decreases drastically when heating up to 200 °C due to the loss of free and bound water[39]. Increasing the temperature of the system further (250 to 300 oC), causes the dielectric constant to further decrease due to the thermochemical cracking of the organic matter. This leads to lower microwave absorption, which can be improved by the addition of microwave absorbing material such as biochar[39].

There is a plethora of microwave-assisted pyrolysis processes in the literature so only a few will be highlighted here. In a recent study by Parvez *et al.* conventional pyrolysis of gumwood was compared to microwave-assisted pyrolysis for gas and char production[40]. For each investigative temperature (600, 700 and 800 oC), the energy and exergy rates for the pyrolytic char and gas were higher for the MAP. Improved performance was seen with the MAP, whereby the pyrolysis system efficiency (PSE) was found to be 13.5% higher when compared to the conventional pyrolysis. Furthermore, 15% more hydrogen was produced in the MAP process[40]. A schematic showing the hydrogen production system based on pyrolysis, was designed by the authors and is shown in Figure 3 below.



**Figure 3. A bio-H2 production system based on pyrolysis along with a co-products strategy.[40]**

In MAP processes, yields of bio-oil and syngas as well as selectivity towards certain products are dependent on the atmosphere and presence of a catalyst. For example, the selectivity of MgCl2 towards furfural production under microwave conditions was observed by Ravikumar *et al.*, whereby the furfural content in the bio-oil from corncob increased to 15% from 3.53% in the bio-oil. The furfural content was the only one to increase when adding MgCl2[41].

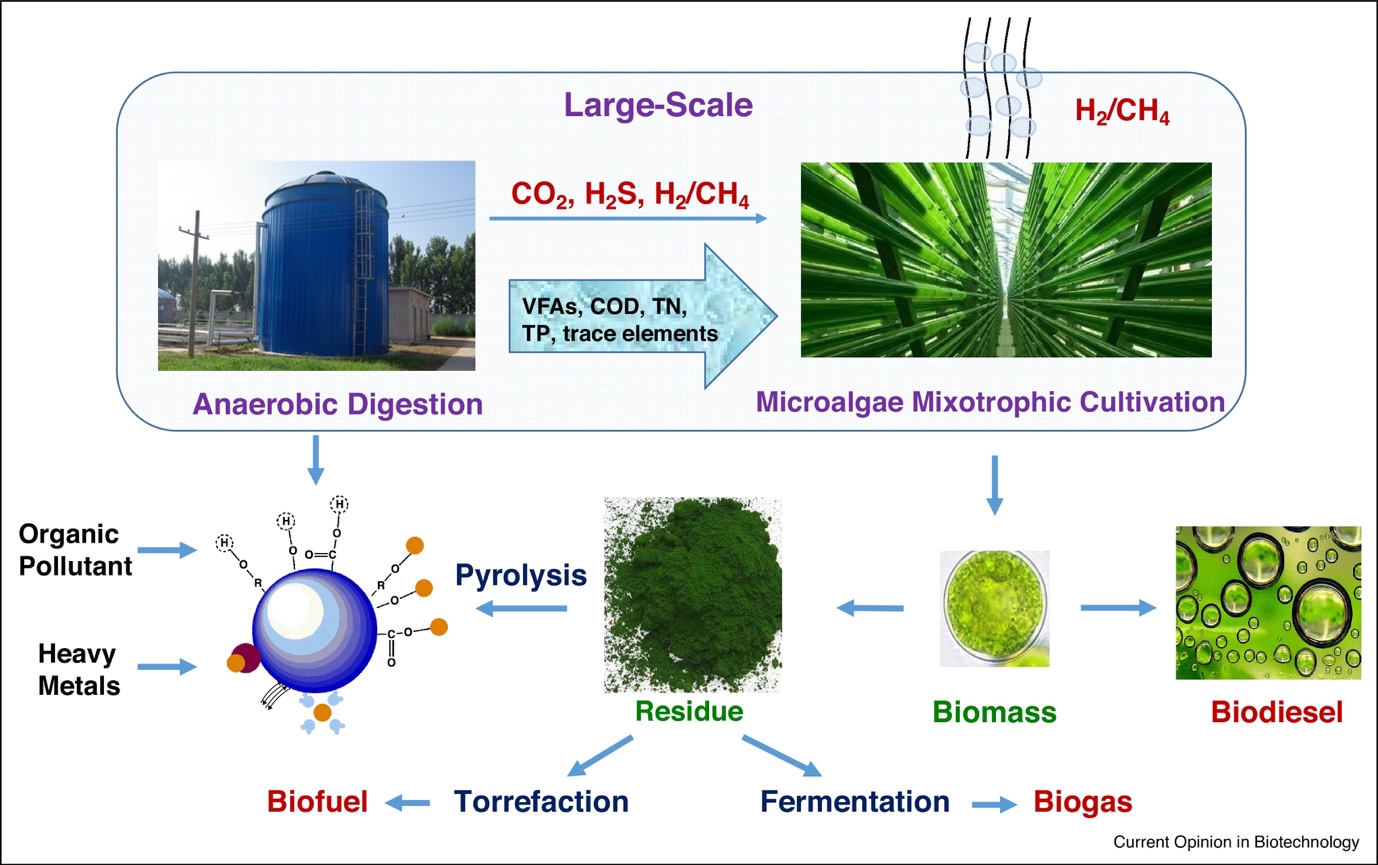
When considering the application of microwave pyrolysis processes, it is important to assess the scalability of the process. A recent study by Salema *et al.* investigated the scale-up of the pyrolysis process (from g scale to kg scale) using corn stalk briquettes[42]. The key parameters looked into were biomass loading and microwave power, both of which affected the final product yields (bio-oil, char and gas). Interestingly, the temperature of the process increased not only with MW power but also with biomass loading. The bio-oil yield increased with both power and loading (with a highest content of 19.6%). In terms of elemental composition, there was little effect of MW on the biochar, however the sulfur content increased with an increase in biomass loading. Good heating values were obtained for the biochar using optimized conditions (32 MJ/kg)[42].

Finally, coupling MAP with other technologies could lead to improved yields of certain products. Bouxin *et al.* recently demonstrated that coupling of MAP with steam distillation of agricultural residues led to a significant increase in both selectivity as well as yields of polysaccharide-derived products such as levoglucosenone (LGO) in a biorefinery setup[43]. Using wet hemicellulose depleted barley straw, approximately 66% of LGO was successfully steam distilled and isolated from the MAP process leading to a combined production/separation process[43].

Similar thermochemical techniques such as liquefaction using microwaves have been applied to biomass in a biorefinery setup. The microwave-assisted alcoholysis of corn stover was conducted by Zhang *et al.* to produce ethyl levulinate (EL)[44]. EL is of significant importance as a promising bio-derived platform molecule as well as a fuel additive (lower sulfur content, high lubricity and better cold-flow properties). Reaction conditions were optimized using response surface methodology, with highest conversions (58.1 mol%) obtained using 190 oC, 30.4 mins, a liquid-to-solid mass ratio of 15 g/g and 2.84 wt% sulfuric acid catalyst. The reaction time for the microwave-assisted process was significantly shorter than conventional heating – 30 mins vs several hours[44].

**Anaerobic Digestion:** Anerobic digestion (AD) of bio-available feedstock by bacteria to give both a source of bio-methane for combined heat and power generation and a solid digestate rich in nitrogen and phosphorous which can be applied as a fertiliser has already been widely implemented. However, AD represents a loss of useful functionality and as such it should be applied to feedstocks with little other option for valorisation. One growing area in this field is co-digestion of nitrogen rich waste such as manure or waste water sludge (sewage) with a carbon rich source to improve overall methane production. Xie *et al* showed that mono-digestion of paper waste, sewage sludge or food waste gave methane yields of 157, 159 and 652 ml g-1 respectively. However, co-digestion of sewage sludge with either paper waste or food waste at a 1:1 *v/v* resulted in increased yields of 368 and 799 ml g-1 respectively [45].  Similarly, two studies published within 3 months of one another showed that co-digestion of corn stover (complex carbon source) with manure (high nitrogen content) is significantly improved upon by the inclusion of a small amount of fruit waste (readily available sugars)[46, 47].  In both studies, although the methane yield improved with the addition of fruit waste, the most significant development was the greater stability of the microbe community in terms of variety of bacteria and tolerance to inhibitors. Such studies have not only been carried out at laboratory scale, a recent publication using a 2000 m3 working volume continuously stirred tank reactor anaerobic digester in Treviso, Italy showed the benefits of co-digestion. Here the liquid squeezed fraction of the organic fraction of solid municipal waste (OFSMW) was combined with waste water sludge at roughly a 1:1 loading based on volatile solids content, increased methane yields by between 97 and 360% compared to sludge alone[48].  As this work was carried out over a 2 year period and with cost/benefit analysis taking into consideration all the factors in running the plant, co-digestion was shown to benefit the process by €81.3 ton-1 OFSMW.

Further advances in AD that progress it towards a significant process in an integrated bio-refinery model are the production of a greater variety of products. Two stage AD allows for the co-digestion of food waste, glycerol and sludge to give both methane and hydrogen[49]. Here a first stage digester at a pH of 5.5 using a heat shocked inoculum obtained from a commercial municipal sewage treatment plant gave rise to hydrogen production. The effluent from this step was then neutralised to pH 7 and incubated to then give methane as product. The relative gases were obtained in yields of 180 and 340 ml g-1 for hydrogen and methane respective. Another pathway of note is the production of volatile fatty acids (VFAs) as major product as opposed to methane, from waste water. By changing the pH at which AD occurs, alongside the use of membrane separation and solvent extraction allows for selective production of different VFAs[50]. Yields here are typically high, around 0.5 g g-1 feed, with acetic, propionic and isobutyric acid as the most common VFAs. Although both hydrogen and VFAs can be directly combusted for energy generation, they would have greater impact and more profitability being utilised in bio-derived synthetic pathways as part of an integrated bio-refinery model. A final advance towards maximum utilisation within an AD plant is the production of microalgae. Here AD effluent is used to produce microalgae which in turn is a source of lipids for bio-diesel production as well as carbohydrate for further processing, as shown in Figure 4 below[51].

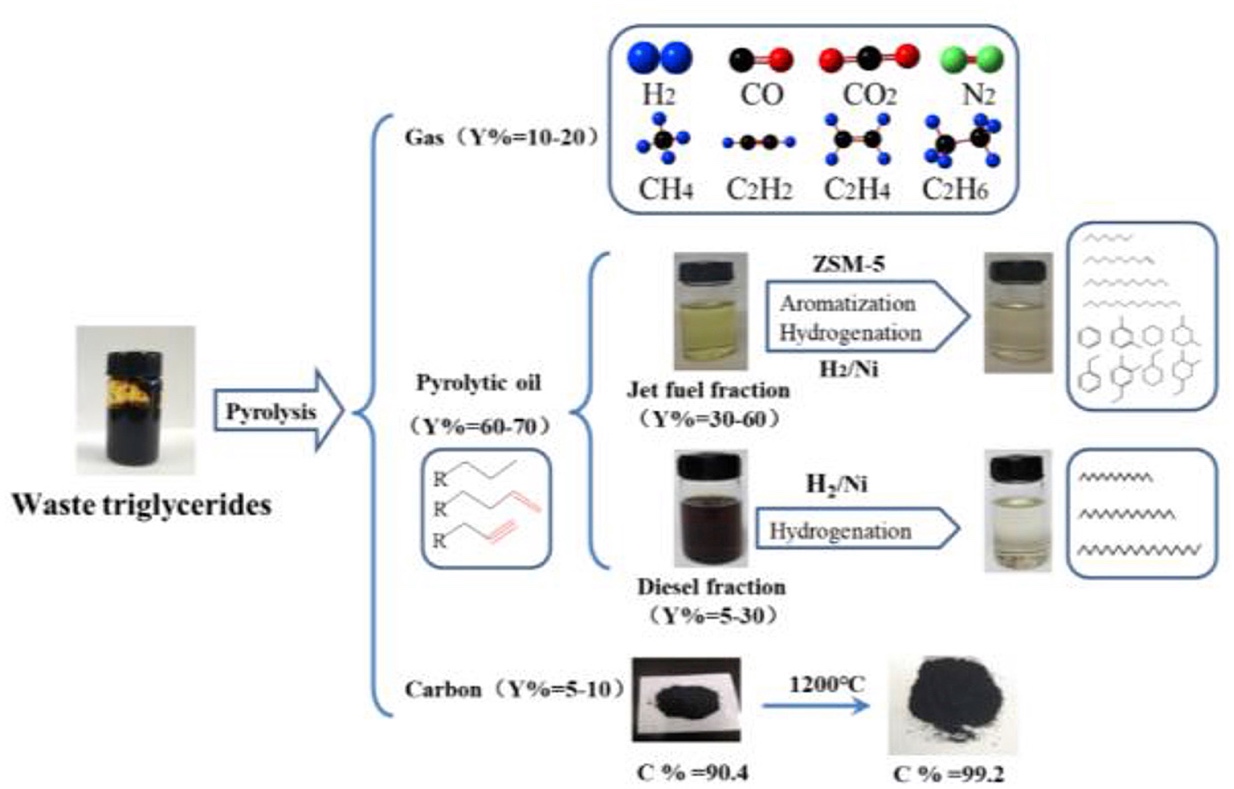


**Figure 4. Concept of an integrated microalgae biorefinery with anaerobic digestion. *Reprint with permission from [51]* Chen Y-d, Ho S-H, Nagarajan D, Ren N-q, Chang J-S. Waste biorefineries — integrating anaerobic digestion and microalgae cultivation for bioenergy production. Current Opinion in Biotechnology. 2018;50:101-10. Copytright Elsevier 2018.**

**Catalysis**

The use of catalysis in a bio-refinery concept can be split into two main fields, those of bio-catalysis and chemo-catalysis.  **Bio-catalysis** here is principally concerned with conversion of biomass into 2nd generation free sugars followed by fermentation to give platform molecules. Pre-treatment of eucalyptus with a deep-eutectic solvent consisting of lactic acid and choline chloride resulted in the separation of the lignin, cellulose and hemicellulose fractions, with temperature playing a crucial role. Enzymatic hydrolysis improved from 9.6% with the untreated biomass, up to 94.3% when pretreatment was at 110 °C. At higher pretreatment temperatures, there was greater removal of lignin and hemicellulose but reduced hydrolysis yields, probably as a result of reduced surface area[52].  Sugars can be applied in fermentation to established products such as ethanol, butanol, lactic acid *etc.* but recent advances towards other platform molecules are broadening interest. The highly versatile itaconic acid has been obtained in significantly higher yields by combining reactive extraction *via* esterification or back extraction in trioctylamine methyloctanoate systems. These approaches allow for continuous recovery of the product in a single unit operation in high yield and purity. Another compound of interest with applications in antibiotic synthesis and as a moisturiser in the cosmetic industry is butane-1,3-diol[53].  This has required the engineering of entirely novel pathways, with recent work showing a still modest yield, but representing a 5 fold increase on those reported previously[54].

**Chemo-catalysis** focuses principally on taking the output of a process in a bio-refinery and upgrading it to a higher value product. Starting from sugars, pathways to 5 member rings such as HMF as a key intermediate are already well established. Routes are now looking to further exploit this chemistry such as continuous conversion of furfural to 6‐hydroxy‐(2*H*)‐pyran‐3(6*H*)‐one in 94% yield (its self a highly functionalised platform molecule) utilising a titanium silicate catalyst along with hydrogen peroxide in ethyl acetate and ethanol, followed by ruthenium on carbon hydrogenation in flow to give pentane‐1,2,5‐triol in 92% yield[55].  Another area of interest is in the field of aviation as there is currently no alternative to high energy density liquid fuels for long haul flights. As such bio-derived version are required for this sector to decarbonise. A recent bio-refinery model has taken low quality, viscous waste triglycerides and/or plant oils and applied a two-step process in order to yield a range of products, indicated in Figure 5 below. Initially the oil is pyrolysed, with the heavy fraction yielding 5-15% coke and 10-25% of uncondensed gas which is combusted as part of an energy recovery mechanism. The 65-80% of liquid hydrocarbons are fractionally distilled, with the lower boiling point materials giving a green diesel while the more volatile component undergoes a one pot catalytic conversion in the presence of zeolite ZSM-5 promoting considerable aromatisation, followed by hydrogenation in the presence of Raney nickel to convert most aromatics to cycloalkanes, the combination of which is an ideal jet fuel[56].



**Figure 5. Bio-refinery model showing the conversion of viscous waste triglycerides and/or plant oils *via* a two-step process in order to yield a range of products using catalysis. *Reprint with permission from [56]* Xu J, Long F, Jiang J, Li F, Zhai Q, Wang F, et al. Integrated catalytic conversion of waste triglycerides to liquid hydrocarbons for aviation biofuels. J Clean Prod. 2019;222:784-92. Copyright Elevier 2019**.

**Conclusion and Future Outlook**

The bio-economy has become a leading initiative in many regions encouraged by legislation, incentives and research. The emergence of the circular economy is very consistent with this especially when biorefinery feedstocks are wastes and products are fully recyclable or biodegradable. Certainly our experience with bio-fuels has taught us to be very careful over the choice of feedstocks and that true sustainability goes far beyond using renewable resources. An increasing emphasis on waste feeds will also help to solve the increasing problem of pollution including food waste. We must also ensure that the technologies of future biorefineries are themselves highly efficient and of low environmental footprint. The traditional chemical industry was based on non-renewable feedstocks and often inefficient, wasteful and dangerous processes. The biorefinery offers us a unique opportunity to make a major step change and provide future societies with genuinely green and sustainable products.

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