Design and scale-up challenges in hydrothermal liquefaction process for biocrude production and its upgradation

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ABSTRACT

Renewables are going to play an important role in meeting the greenhouse gas (GHG) emission targets to mitigate the effects of climate change. Most of the bioenergy production processes available today can be broadly categorized into two types of technologies - biological and thermochemical processes. Worldwide, the major practiced methods are Combustion/Incineration, Pyrolysis, Gasification, Anaerobic digestion, Fermentation etc. These methods have their own benefits and limitations based on their capability and capacity to process various feed stocks, energy efficiency, operational challenges, product quality and economics. Hydrothermal liquefaction (HTL) process is one such method, which has recently attracted attention of many scientific and practicing community across the world on various platforms. HTL process has the ability to convert all kinds of biomasses to crude bio-oil, which is comparable to fossil crude oil and can be upgraded in existing refinery set-up. Although it has significant benefits over other conversion technologies, HTL process is yet to be commercialized. Several technical and operational challenges have been reported in literature that need to be addressed for successful scale-up and design of continuous scale HTL process. Large number of review and research articles pertaining to batch and pilot scale are available on the process and product development aspect of HTL process. However, limited information is available on the design and scale-up issues that are envisaged in the scale-up of HTL technology. This review article identifies various design, scale-up and operational challenges in HTL technology and proposes potential ways to mitigate those challenges.

Introduction

Bioenergy, being the largest form of renewable energy in use today and accounting for more than 65% of the total renewable energy supply globally, is poised to play a major role as future source of energy. Biomass derived energy and products will be critical in meeting goals to combat climate change with effective energy transition [1,2]. Bioenergy applications in form of biofuels are predicted to be key components to decarbonize the future energy economy. Importance of biofuel is especially evident in transport sector applications such as aviation, shipping and long-haul road transport, where biofuels might be the only option for decarbonization for years to come. Biomass, bioenergy and biomass derived chemicals will provide a sustainable source for fuel and feedstock.

Hydrothermal liquefaction (HTL) is a thermochemical conversion

that converts various biomass feedstocks into liquid fuels by processing in a hot, pressurized water at near subcritical conditions -for sufficient time [3]. Original bio-based fractions are broken down and deoxygenated substantially at these conditions in HTL. The newly formed polar organic compounds are contained in the effluent aqueous phase and are water soluble, whereas non-polar organic compounds form liquid bulk fraction termed crude bio-oil (CBO). Biomass slurries with solid loading in the range of 5%–30% w/w dry biomass content, in the presence or absence of catalysts are processed in HTL, resulting in high carbon efficiencies and energy recoveries in the crude bio-oil. HTL has been successfully demonstrated for a variety of feedstocks including lignocellulosic [4,5], marine [3,6,7], waste biomasses [5,8,9] and their co-processing [10]. Liquefaction reaction mainly comprises of a) Depolymerization of biomass to form water soluble monomers, b) Degradation of monomer by dehydration, deamination, and decarboxylation

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reaction, c) Re-arrangement of reactive fragments to water insoluble crude bio-oil, d) Polymerization at prolonged reaction time to form char. The carbon content of initial biomass is partitioned in four liquefaction products: the water insoluble crude bio-oil, water phase containing polar components, the gaseous phase mainly constituted by CO_2, and the solid residue consisting char and ash. Crude bio-oil produced through hydrothermal liquefaction process is similar to petroleum crude and can be upgraded to the whole distillate range of petroleum derived fuel products.

Although HTL has significant benefits over other conversion processes, its commercialization remains a challenge. For successful scale-up and design of continuous scale HTL systems, seven primary technical challenges needs to be addressed. These are (i) Feed processing for optimizing solid loading in slurries, (ii) Fouling and increased pressure drop in heat exchangers, (iii) HTL reactor design to avoid solids accumulation and enhance conversion, (iv)Pressure reduction system of the products and heat exchange optimization (v) Substandard fuel properties of crude bio-oil such as corrosivity, (vi) Increased heteroatom content in the crude bio-oil compared to typical refinery crude posing difficulty in upgradation, (vii) HTL by-products utilization. Objective of the article is to review these design and scale-up challenges and present the different solutions that have been developed to counter the most common technical issues in the area of HTL. The review consolidates these design and scale-up challenges and offer independent perspectives to overcome them.

Feed pretreatment, preprocessing

HTL is a feed flexible process and can process any kind of organic biomass such as municipal solid waste; industrial sludges such as black liquor, effluent waste, spent wash; agricultural residue; food waste; etc. in an efficient and effective manner. Various biomass types undergo complex reaction patterns and respond differently to process conditions such as heating rate, reaction residence time, operating temperature and pressure, pH, etc. Slurry characteristics and behavior differs with each feedstock and demands different kind of feed processing equipment and configurations wherein feed is processed into desired range of particle sizes, slurry concentration, homogeneous catalyst loading and solvent addition. Typically, positive displacement pumps are used downstream of feed preparation section to pressurize biomass slurry in the high-pressure heating and reaction section. Industrial scale HTL plant can process the feed in slurry form ranging between 5% and 30% solid concentration. A large variation is seen in the behavior of biomass slurry when it is heated and subjected to pressure in the feed processing section of HTL unit. In order to achieve continuous and uninterrupted operation of HTL and reduce clogging issues, a homogeneous, stable and easily pumpable slurry needs to be prepared with average solid particle size not exceeding 100 μm [3]. Depending on the nature of the feedstock (wet/dry feedstock, presence or absence of lignin), different pretreatment processes shall be required. For example, lignocellulosic terrestrial biomass leads to the formation of hard spherical particles upon milling or grinding. This can cause problems during feeding the slurry in the reactor such as blockages at the pump head, clogging in the check valves, etc. Another issue could be settling of non-homogeneous slurry in the feed section and in the pre-heating section of the unit. Both issues, if not tackled, would lead to pump blockage and would require manually disassembling and cleaning of the pump.

Pre-processing of lignocellulose biomass

Woody/lignocellulosic biomass comprises of hemicellulose, cellulose and the lignin compounds which have rigid structures and are tough to breakdown in HTL process; Additional processing and costs are involved to achieve homogeneity with these feedstock for continuous flow in HTL systems [11]. The woody biomass requires pretreatment for reducing the particle size, removing the contaminants and alkaline treatment to obtain a stable slurry for easy pumping. Dry agricultural waste is also one type of lignocellulose feedstock suitable for HTL processing. Significant quantity of dry agricultural waste available today, mainly comprises of paddy/wheat/maize straws, cotton and soya bean field crop remnants after harvesting and other kind of weeds. For HTL processing, the dry waste is first shredded into smaller pieces of 7–10 mm and then reduced to finer sizes below 30 μm via pulverization. The pulverized fine powder is mixed with water to make homogenous 10% to 20% w/w concentration slurry for HTL. A couple of major challenges with such feedstock are the low bulk density of agricultural waste which makes transportation costly and issues in making pumpable homogenous slurry with water because of significant density difference between the two. Adding organic solvents can be a possible solution to latter issue of homogenization. Alternatively, the co-processing of pulverized agricultural waste with algae can be a feasible solution for making homogenous slurry. Jensen et al. have shown that crude bio-oil yield is around 40–45% in the presence of NaOH as catalyst compared to NH_3 [12]. Processing issues such as increased pressure drops were encountered during the experiments using ammonia as catalyst. This is mainly due to the heavy solid precipitation during HTL reaction. Zhang et al. conducted batch HTL experiments with H_2SO_4 as catalyst in water–ethanol reaction mixture and observed higher oil yield compare to base catalyst for cellulosic type of feedstock. Typically, lignin rich feedstocks show higher yields with base catalysts, whereas for biomass rich in cellulose and hemicellulose acid catalysts have been reported to be more effective [13].

Pre-processing of algal biomass

One of the promising feedstocks for HTL process is algal biomass. Algae biomass contains lipids, proteins, and carbohydrates and can be processed into fuels or other valuable co-products through various chemical, biochemical, or thermochemical process [14–17]. HTL directly converts wet microalgal biomass into crude bio-oil, biochar and aqueous product. It is observed that algal biomass pretreatment could improve the yield and quality of the crude bio-oil produced by disrupting the microalgae cell and enhancing the constituent conversion [18]. Various pre-treatment methods have been tried out for algal biomass. Some common mechanical pretreatment methods include bead milling, high-pressure homogenization, microwave, pulsed electric field, and ultrasonication treatments whereas non-mechanical methods consist of acid or alkali treatment, autoclaving (i.e., pressurized cooking), enzymatic cell lysis, adding ionic liquids, and osmotic shock treatments. It has been reported that these pretreatment methods could boost the yield of crude bio-oil oil while lowering its heteroatom content [19,20]. Therefore, the incorporation of an appropriate pre-processing technique will enhance the production and quality of algal crude bio-oil oil.

Economical processing of algae slurry requires use of high solid concentration that reduces process volume and energy cost. At higher solid loading, these slurries pose challenge in pumping and pressurization due to settling and increased viscosity. Cell rupture in preprocessing section changes the rheological properties of the slurries, which become highly viscous and show irreversible shear thinning behavior [21]. A well-mixed and pumpable slurry is desired from pretreatment section for uninterrupted HTL operation. Shear thinning can be used to reduce the viscosity and increase homogeneity. A large variation is also seen in the behavior of algae slurry when heated and subjected to high pressure in HTL. Slurry viscosity reduces dramatically at elevated temperature near subcritical conditions in HTL.

Pre-processing of municipal solid waste (MSW)

MSW consists of papers, plastics, metals, non-metals, glass, soil, plant and tree waste, food waste etc. HTL requires organic feed with desired inorganic and ash content of less than 10% by wt to avoid system

clogging due to inconsistent slurry and deposition. Also, for smooth processing, the desired particle size in HTL feed is less than 100 μm with solid concentration in the range of 5–30% by weight. Therefore, MSW requires some form of pre-treatment before HTL treatment. In general, large size objects are the first to be removed from MSW before feeding it to the MSW segregation and processing plant. Ferrous and non-ferrous metals are separated from MSW using magnetic and Eddy current separator respectively. The large particles of metal free waste are cut into smaller pieces in the range of millimeters using shredder. These shredded pieces of waste are passed through air density separator which segregates the biodegradable and non-biodegradable content which are collected separately. The biodegradable portion is sent to two stage grinding system where the solid particle size further reduces to less than 500 microns and 100 microns, in the first stage and second stage grinder, respectively. Water is added to the grinders to enhance the grinding process. The grinded slurry is then fed into the expeller/de-watering machine to separate solids from liquids; the organics solid stream consists of very less moisture content while the organics liquid stream consists of solid concentration in the range of 10% to 20% by weight. The solid organics can further be recycled to the expeller to increase the solid concentration in liquid organics slurry if the desired slurry concentration is not achieved with one pass expelling. This output organic liquid slurry forms a suitable feed for HTL system.

Pre-processing of industrial sludge

HTL can be an alternative to traditional technologies for waste management such as disposal and valorization of wastewater sludge. Hydrothermal liquefaction could be an effective technical route for treatment of wastewater sludge for recovery of energy in the form of crude bio-oil. Typically, Sewage or effluent treatment plant sludge after thickening, stabilization and de-watering are sent to landfill which could create a major risk of soil pollution and ground water contamination. HTL is a promising technology which can convert this waste into energy rich resource. Recently, industrial sludges such as oil sludge generated in refinery [22], black liquor from pulp and paper industries [23], biological sludge from common effluent treatment plant [24], etc. have been found to be favorable feedstocks for HTL. STP/ETP sludge generally contains grits/stones/pebbles/metal parts like nuts and bolts which have to be removed through a de-gritting system. The de-gritted sludge is then homogenized in a tank with addition of water (if required) to make 10% − 20% solid concentration slurry to be used as HTL feed. Another promising feedstock is black liquor which is a by-product of the Kraft pulp process. In the Kraft pulp process, lignocellulosic biomass is treated under alkaline conditions (pH greater than 12) at a temperature range of between 433 K and 453 K for 0.5–3 h. About 170 million dry tons of black liquor were produced in 2007, which corresponds to an energy content of 2 EJ. Common practices for dealing with the organic compounds in black liquor is mainly based on drying it and then recovering its energy content by burning it in a recovery boiler. However, more effective utilization would be to convert the organic fraction of black liquor into useful and separable organic compounds. HTL process enables the wet biomass to be treated without drying [23]. However, black liquor contains large quantities of salts such as sodium carbonate, sulfate, magnesium and calcium hydroxide or carbonates [23]. These low solubility salts can cause problems in the process if they precipitate on the hot surfaces of the heat exchangers, preventing heat transfer and causing possible blockages [25]. Therefore, various processes have been recommended and described in literature to separate out these salts upstream of HTL, for instance, continuous filtration [3], semi-continuous salt trap [26], or continuous extraction [27].

Feed pretreatment scheme for scale-up systems

It is critical for commercial scale HTL systems to handle and process various biomass types and ensure continuity of operation particularly during insufficiency of feedstock. The high-pressure section of HTL system, beginning from high pressure pump and including heat exchangers, reactors, solid separation filters, and slurry depressurization system are susceptible to slurry properties, mainly solid loading, particle size and viscosity. Consequently, the design and configuration of feed pre-treatment section is an important aspect. The desirable output from feed pretreatment section is to produce feed in slurry form with solid concentration below 30%, particle size preferably below 100 μm, and viscosity less than 100,000 cp.

Reliance has developed a feed-flexible customized pre-treatment scheme through extensive study and trials on different equipment, configurations, and biomass. The suggested process scheme is designed to handle large variety of biomass and organic waste and is capable of co-processing wet and dry feedstock such as municipal solid waste (MSW), food waste, fruits and vegetable waste, animal manure waste, ETP/STP sludge and dry agricultural waste. The feed-flexible configuration of this system will ensure 100% capacity utilization of HTL plant by ensuring feed security.

MSW is most complex feedstock and hardest to process as it contains lot of unwanted materials and contaminants. Therefore, as a first step- a manual sorting is to be performed where recyclables such as glass bottles, metal cans etc. and big size waste items is separated out. The remaining stream than passes through eddy separator to further remove small metal contaminants. Once free of recyclables and contaminants the size reduction is performed in primary shredder. Some dry lighters such as small plastics and papers are than separated out from heavier organics in air density separator. The remaining wet organic heavy fraction is than further reduced in size using wet secondary shredder. Most of the inherent moisture content in mixed MSW is bound with organic waste and therefore the wet organic fraction contains moisture in the range of 60–70%. The shredded and reduced organic stream is then grinded in two-stage grinding system to further reduce particle size and improve homogeneity.

The other wet organic biomass or waste such as algal slurry, raw vegetables, cooked food waste, animal manure waste, ETP/STP sludge can be added in grinder system to co-process with MSW. Dry biomass and waste such as agricultural residue, lignocellulosic biomass, wood chips and forestry residue are required to be processed in additional shredding and pulverizing system, before introducing to grinder system for co-processing. Addition of organic solvents and HTL aqueous product recycle can be carried out at this step to achieve the desired solid concentration, improve pumpability, and enhance HTL crude bio-oil yield. The grinded slurry is then sent to homogenizer system where further homogenization is performed and viscosity is reduced through shear-thinning. This ready feed slurry is then introduced to HTL high pressure section.

Feed preprocessing

Composition of crude bio-oil could be impacted by several factors, ranging from feedstock chemical composition to HTL operating parameters. For example, separation of protein fraction prior to HTL or milder operation conditions will result into crude bio-oil with lower nitrogen content [3]. Jazrawi et al. extracted nitrogen (up to 50 w.t%) from *Chlorella* biomass before the main HTL [28]. By this pretreatment, the nitrogen concentration in the produced crude bio-oil was decreased by 55% at the expense of crude bio-oil yield (12.7 *vs.* 24.7 wt%), compared to the direct HTL. In a separate study, Huang et al. decreased the oxygen and nitrogen contents of crude bio-oil from microalgae by the addition of a pretreatment step (225 °C, heating rate 5 °C min^{-1}, 50 min). Interestingly, both calorific value and yield of crude bio-oil had direct relationships with the pretreatment time and were respectively increased, calorific value from 34.9 to37.1 MJ. kg^{-1} and yield from 26.5 to 34.3 wt% when processing time was prolonged from 10 to 50 min [29]. Alternatively, the elevation of reaction temperature, for example to 350 °C in the case of HTL of *Scenedesmus* sp., increased the contents of

carbon (considerably) and nitrogen (slightly) [30]. Moreover, the process produced highly deoxygenated crude bio-oil with higher heating value (i.e., calorific value) as the result of the increase in carbon content and the decrease in oxygen content.

Hydrothermal liquefaction (HTL) process and design challenges

Feed pressurization

Pressurization of the slurry is performed by the high-pressure feed pump and the system pressure can be adjusted with a back-pressure regulator or pressure control valve. Positive displacement pumps such as diaphragm pump, piston pump, and rotary piston pump can be used in commercial scale or pre-commercial scale plant. Syringe type pump is preferred at bench scale or pilot scale unit. Feeding section may sometimes consist of two pumps in series. The first pump is a progressive cavity pump or shear thinning pump, such as gear pump, stator rotor pump, etc. This pump provides continuous recirculation of the slurry in the feed tank to ensure the homogeneity of the slurry thereby minimizing settling of the feed slurry. The same pump provides a steady flow to the second stage high-pressure pump at slight overpressure ($\sim$2–3 bar). In the high-pressure pump, there are certain common pumping problems such as issues in developing the desired pressure and frequent fluctuations in the system pressure. Misalignment of sleeve from the axial position, damage of the diaphragm, calibration of hydraulic valve, damage in the hydraulic oil refill valve seat surface are some of the common operational reasons for pumping issues.

Biomass heating

Heat exchangers are an integral part of Hydrothermal Liquefaction (HTL) as the process conditions required for HTL are near to subcritical condition of water (300 – 350 ^{0}C temperature and 180–210 bar pressure). With the requirement of bio-refinery, a completely new field has been opened for heat exchanger design where the feed properties are not completely known, just like the scenario at the beginning of petrochemical or refining sector, and a detailed analysis is required in heat exchanger field. Various organizations working on biomass have tried conventional heat exchangers. However, due to viscous, settling and charring nature of biomass, a lot of limitations have been observed in utilization of conventional heat exchangers for biomass applications at high temperatures [9].

Various thermo-physical properties such as viscosity, density, heat capacity, fouling factor etc. play a vital role in heat exchanger design. However, biomass slurry is not a conventional feed and detailed analysis is not available in literature for various biomass slurries. The thermo-physical properties are not readily available in database of simulation software such as ASPEN PLUS, HTRI etc. Additionally, wide variation in the biomass slurry composition makes it difficult to standardize these thermo-physical properties.

Variation of these properties may result in heat exchanger over or under design, thus detailed analysis is to be performed prior to commercialization. Typical thermo-physical properties of biomass are shown in the Table 1.

Viscosity not only has effect on pressure drop [31] across the heat exchanger, but also indirectly affects the heat transfer due to varied-Reynolds and Prandtl no. of the fluid. Thus, viscosity estimation is

Table 1
Thermophysical properties of typical algal biomass.

Sr. No.	Parameter	Value	UOM	Ref.
1	Biomass conc.	10–30	% wt by wt	
2	Density @30 ^{0}C	980–1100	Kg/m3	[45]
3	Viscosity @30 ^{0}C	10,000 – 100,000	cP	[21]
4	Fouling factor	0.02–0.05	hr-ft2-F/Btu	

critical and can be measured using viscometer at lab scale. However, during continuous trials, biomass slurry is likely to be impacted during pressurization, shear thinning, heating etc. which modifies biomass slurry behavior and thereby affects the viscosity at operating conditions. Biomass slurry viscosity estimation can be achieved with the help of pressure drop experimental data from bench/pilot scale using equation (1).

$$\frac{\Delta P}{L} = \frac{f * \rho * v^2}{2 * d} \tag{1}$$

where $\Delta P/L$ is pressure drop across length (kg/m^2 s^2), f is fanning friction factor (-), ρ is process fluid density (kg/m^3), v is process fluid velocity (m/s), d pipe inner diameter (m). Overall heat transfer coefficient is very critical for heat exchanger design and depends upon the MOC, fluid properties etc. Heat transfer across heat exchanger depends directly on overall heat transfer coefficient and can be represented using equation (2).

$$Q = U_{clean} A \Delta T \tag{2}$$

where Q is heat duty (W), U_{clean} is overall heat transfer coefficient in clean condition (W/m^2 K), A is heat transfer area (m^2), ΔT is temperature gradient across hot fluids (K). The overall heat transfer coefficient changes with time due to fouling of heat exchanger surfaces. The fouled heat transfer coefficient is represented as U_{dirty}. Heat transfer across the heat exchanger after fouling can be represented using equation (3).

$$Q = U_{dirty} A \Delta T \tag{3}$$

where U_{dirty} is overall heat transfer coefficient in fouled condition (W/m^2 K), A fouling resistance [32] is thus defined over an average run length of the heat exchanger and is defined as difference in heat transfer coefficient during clean and dirty condition of heat exchanger as depicted in equation (4).

$$R_f = \frac{1}{U_{dirty}} - \frac{1}{U_{clean}} \tag{4}$$

where R_f is fouling resistance (m^2 K/W). Fouling factor data is critical for effective heat exchanger design and achieve required process temperatures even during fouled conditions. Nevertheless, use of incorrect fouling factor may also lead to heat exchanger over-design or insufficient heat transfer surface area.

Heating of biomass slurry in HTL process from ambient to sub-critical condition requires controlled heating due to charring nature of the fluid. Similar to a refinery or petrochemical processes, various exchanger types can be used in HTL process, such as shell & tube, spiral heat exchanger, double pipe heat exchanger, etc. Type of heat exchanger to be used can be decided based on the rate of heat transfer, which depends upon the thermal and physical properties of the process fluid, such as viscosity, specific heat, fluid velocity in pipe, which in terms governs the fouling factor. Typically, fouling factor of 0.002–0.005 m^2.h. C. KCal^{-1} and pipe velocity of 10–20 cm. s^{-1} can be used for exchanger design, which is derived using Reliance in-house experimental data on various biomass feedstock. A spiral heater is a compact heat exchanger and would provide greater turbulence for same velocity. However, it is difficult to clean and thus may not be appropriate choice for HTL slurry, which has a fouling and settling nature. Therefore, straight tube heat exchangers such as double pipe, shell and tube exchanger etc. are more appropriate for feed preheating as they can be easily cleaned. Once heat exchanger type is selected, the next challenge is to decide the tube size and number of exchangers. Fluid viscosity and settling velocity plays vital role in determining the tube size. Highly viscous nature of the biomass slurry demands for larger tube size whereas velocity requirement demands for a lower tube size. Irrespective of the throughput of the unit, biomass slurry flow will remain in laminar or very low turbulent flow resulting in decreased overall heat transfer coefficient and an

increase in the area required for heat transfer. Overall heat transfer coefficient at fouled conditions remains in the range of 36–88 Btu/hr-ft2-F (204–499 W/m2-K) based on Reliance in-house trials conducted at bench and demo scale HTL plants. Heat integration is another option to conserve 60–70% of sensible heat by utilizing the heat content of product stream as heating medium in the feed preheater.

In case of very high temperature gradient between hot and cold fluid, charring of HTL biomass is observed. This charring effect could limit the approach temperature across exchanger, thereby increasing the number of exchangers required in series. Therefore, one of the major foreseeable problems in commercialization of HTL process are frequent fouling and charring in heat exchangers. Charring frequently results in sudden choking due to the dislodging of lumps of charred material in the process side pipe. Charring and fouling impact can be mitigated by properly maintaining heat exchanger skin temperature. In the case of algal slurry cultivated in saline water, there is possibility of iron leaching in the process stream when stainless steel (SS316/304) is used as material of construction for exchangers. Selection of high-grade metallurgy on process side such as Inconel or super duplex based on the operating temperature range in the exchanger could eliminate the problem of corrosivity and iron leaching associated with the biomass slurry.

HTL reaction section

Hydrothermal liquefaction is a thermochemical process that converts any wet organic biomass and waste to liquid fuel and useful by-products. It has certain advantages over the conventional thermochemical process, such as elimination of feedstock drying, increased reaction rate, and higher product yields and energy efficiency. HTL exploits the property of hot compressed water (200–400 ^{0}C and 50–250 bar) to convert biomass to liquid biofuel and other value-added products. At these conditions, water remains in a liquid sub-critical state and the thermo-physical properties are vastly different compared to water at ambient conditions. The viscosity and dielectric constant of water decreases, while the ionic product increases significantly, and it behaves like nonpolar component at these condition that leads to an increase in solubility of organic molecules. Primarily three reaction pathways have been suggested [34,35,10,36] to contribute in HTL process. Fig. 1 presents the likely HTL reaction pathways at the molecular level [52]. These are, depolymerization of biomass, hydrolysis and decarboxylation to breakdown monomers and form water-soluble compounds such as acids, phenols and alcohols which forms HTL aqueous phase, and repolymerization reactions to generate energy rich products such as crude bio-oil and carbonaceous solids called char that separates out from water phase. The HTL product yields are affected by type and composition of biomass, solid loading, process temperature and residence time.

Biochemical composition of feedstock significantly influences crude bio-oil yields in HTL process. Typically, all biomass is composed of Carbohydrates, Proteins, Lipids, and lignin fractions in varying percentage. Forest and agricultural derived biomass are rich in carbohydrates present in form of cellulose and hemicellulose forming up to 50% by weight and remaining majority being Lignin. Other biomass and waste such as algal biomass, MSW organics and food waste are richer in Lipids and proteins fractions [37,38,39]. At elevated temperatures above 250 °C, proteins are first hydrolyzed and degraded into hydrocarbons, amines, aldehydes, and acids [33]. As a general trend, HTL crude bio-oil yields are higher with lipids followed by Proteins and Carbohydrates and higher carbohydrates in biomass demands higher process temperature [40–41]. Reaction temperature and residence time are two other important parameters that significantly affect crude bio-oil yields and requires optimization. Temperatures beyond 350 °C and increases residence time promote decomposition of crude-bio-oil and repolymerization reactions that leads to increased formation of gases and char [39,42].

Reactor design, challenges and development status

HTL reactions have been studied extensively in literature with various feedstock, however, most of them are done in lab batch scale
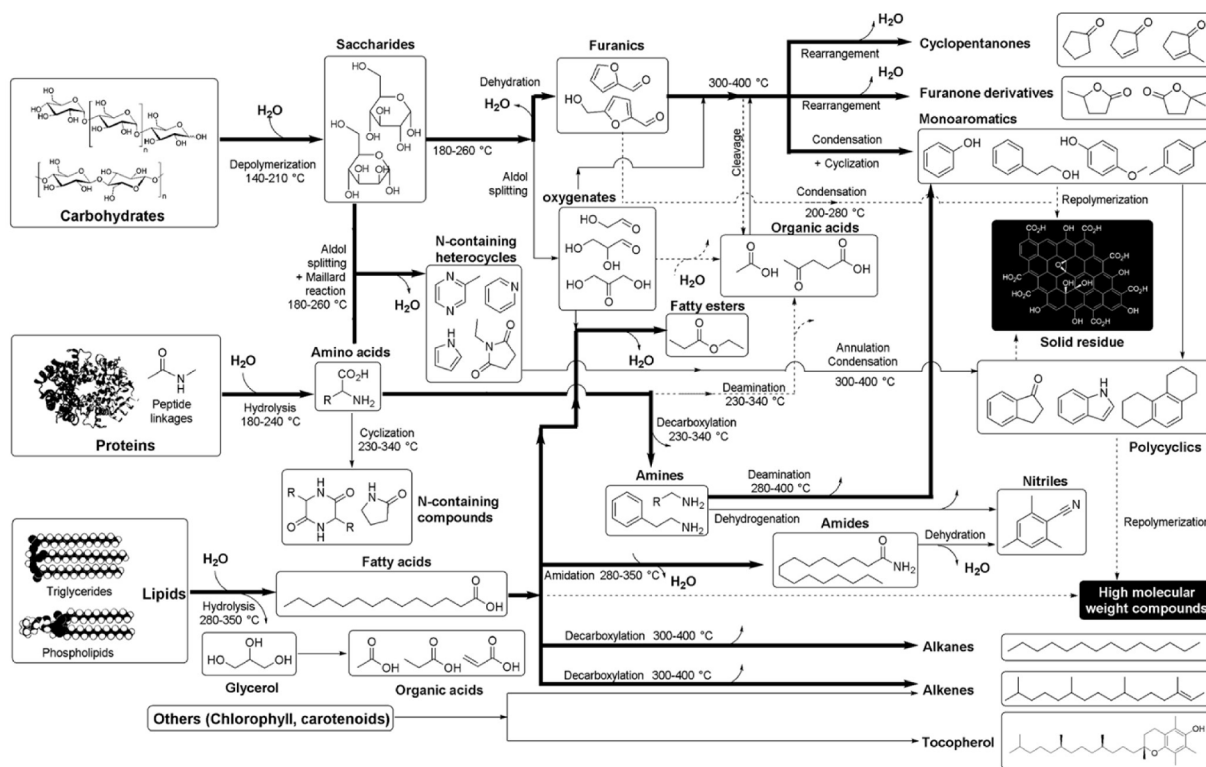

Fig. 1. Hydrothermal liquefaction reaction pathways: a molecular perspective [52].

reactors. In batch reactors, biomass feedstock is loaded at desired concentrations with or without catalyst and reaction temperature and residence time can be controlled precisely. These reactors help in quick screening of various feedstock and achieve optimization of the process conditions. However, scaled-up commercial HTL systems will require continuous reactor systems capable of effectively controlling reaction temperature and provide flexible residence time. Moreover, continuous reactors allow energy recovery which increases overall process efficiency and make the process economically feasible [28].

At Reliance, HTL process journey evolved from batch reactors (4 ml, 300 ml, 2000 ml) and scaled-up the process to bench and demo scale continuous reactors with flow rates in the range of 2–80 L. h-1, producing more than barrel a day of crude bio-oil. To the best of our knowledge, the demo scale plant is one of the largest continuous HTL system in operation today in Industrial environment. This continuous system consists of a high-pressure pump feeding system, a series of exchangers to achieve preheating and reaction temperature, two 14 L continuous stirred tank reactor in series and a high-pressure solid separation system. The demo system can process algal biomass, MSW organics and food waste, ETP/STP oily and bio sludge at variable operating conditions 200–370 °C, 150–220 bar and 10–30 min of residence time and has been operated for more than 1500 hrs producing more than 30 barrels of crude bio-oil till date. Much of the operational challenge in this continuous reactor system has been in heating the biomass slurry with frequent charring and choking issues in exchangers especially in range of 150 °C to 300 °C, which was resolved by modifying to a staged heating design with an option to control heating rates effectively. Other observed issues with stirred tank reactor design were agitator seal leakage and deposition of solids at reactor bottom and sticking at sides, eventually filling up the reactor and resulting in reduced volume and reaction residence time. Seal leakage issues can be resolved with suitable MOC selection for these process conditions. Solid settling in stirred reactors can be eliminated with good mixing and appropriate agitator design. The bench scale system at Reliance utilizes a continuous stirred tank reactor for preheating algal feedstocks followed by a plug flow reactor, which effectively eliminates the above discussed issues.

At commercial scale, plug flow reactors will provide additional flexibility to optimize residence time for different biomass feedstock characteristics, maximizing yields and improve quality of crude bio-oil. This can be achieved by having identical tubular sections of equal residence time, which can be taken in-line or bypassed to achieve required residence time. Solid settling could also be minimized by maintain healthy flow velocity and minimizing bends.

An important aspect of continuous reactor design development for HTL process is developing a robust product separation technique. Separation of hot and pressurized mixed product stream from HTL reactor with high solids and ash content is one of the most difficult design challenges associated with continuous HTL systems worldwide. The carbonaceous solids, unconverted biomass, ash and inorganics can cause blockage issue in reactor downstream systems consisting of depressurization and product separation equipment. The fine solid particles of char and salt deposit in pipes and damage the back pressure regulator at downstream and hence required to be removed after reaction. Reliance bench and demo scale system utilized high pressure filter after reaction section to capture the char and solids. The deposited solids on filter are removed frequently using a highly automated blowdown sequence. However, the system goes through high pressure and temperature fluctuation during blowdown and requires some time to stabilize the reaction process conditions. In addition, the system needs shutdown when the filters are choked after multiple blowdowns. Industrial scale-up design for solid separation could utilize two or multiple parallel high pressure filtration system. This design will help in process continuity during solid removal and blowdown of one of the filters, during which time the other filters will be taken in line. The changeover and cleaning sequence can be completely automated using on–off valves.

Some other steps to mitigate the clogging issues can be reducing the ash and impurities in feedstock, effective pre-treatment of biomass to reduce particle size and increase pumpability, and increasing the pipe diameters in HTL system.

Some of the research work performed on continuous HTL reactor development is described here. The University of Sydney group developed a 2 L plug-flow reactor system with flow rates in the range of 15–30 L. h^{-1} and residence time up to 5 min. The slurry is preheated till 170 °C before the reactor, where final heating is performed to reach reaction temperature. The system is claimed to be operating without any clogging issues with maximum run of 2 hrs [3,28]. The Pacific Northwest National Laboratory (PNNL) group HTL system uses both continuous stirred reactor and plug flow catalytic reactors to avoid the plugging issues [43]. The University of Illinois at Urbana-Champaign (UIUC) has developed stirred tank reactor system capable to process up to 20% w/w solid loading and uses agricultural biowaste, swine manure and food processing waste as feedstock [44]. Several different studies have been published in the literature describing continuous HTL systems worldwide. Table 2 describes the reactor and product separation techniques in development and employed in continuous HTL processes along with typical operating conditions.

Characteristics of HTL crude bio-oil

HTL process typically converts more than 50% of the biomass (ash free and dry) to organic fraction crude bio-oil and approximately 65–75% of the carbon present in the feedstock goes into the crude bio-oil. HTL crude bio-oils in nature are usually semi-liquid, viscous, dark-colored and have a smoky smell. Usually, the components present in the crude bio-oil are acids, alcohols, aldehydes, esters, ketones, phenols, and guaiacol, besides a few hydrocarbon and nitrogen containing species [49]. Also, the viscosity of crude bio-oils can be upto 10–10,000 times higher than that of diesel and biodiesel [50]. Moreover, heating values are also slightly lower than those of conventional fuels and biodiesel. These properties make direct application of HTL crude bio-oil as conventional transportation fuels difficult, apart from marine applications [51].

The crude bio-oil generated from HTL is known to be unstable at room temperature and can also contain significant weight percent of nitrogen and oxygen, besides some amount of sulphur [53,54]. The quality of crude bio-oil produced is primarily dependent on the feedstock being processed and hence feedstock which are hydrocarbon in nature, such as oily/refinery sludge and plastic waste, typically produce crude bio-oil which is low in ash content and has very low heteroatom content and negligible inherent moisture content. This, in turn, makes the oil easily upgradable discussed in later sections. On the other hand, crude bio-oil produced from feedstock such as algae, MSW or food-waste tends to have a relatively higher ash and inherent moisture content as well as higher heteroatom content. Even though HTL is a feed flexible technology and can process various feedstock, the crude bio-oil obtained from these feedstocks varies with their physical properties and chemical composition (Table 3).

For such feedstock, the water and oxygen content in the crude bio-oil is higher than that of refinery crude oil and desired transportation fuels resulting into lower heating value. In addition to this, concentration of nitrogen is also higher than that of refinery crude. Typically, the TAN of the crude bio-oil is high which in turn leads to high corrosivity. The acidity and corrosiveness are the result of a considerable amount of fatty acids present in the crude bio-oil which contribute also to a higher TAN (total acid no.). Also, side reactions such as polymerization occur during the storage period at ambient conditions and evaporation causes a slow increase in the already high viscosity [56]. Hence crude bio-oil from different feedstock requires different upgradation strategies. Complete compositional analysis of HTL crude bio-oil, at the molecular level, is essential for feedstock selection and process optimization. Sudasinghe et al. reports a detailed compositional analysis of HTL crude bio-oil by

Table 2
Summary of continuous HTL reported in the literatures.

Plant Location	Capacity (Kg/h)	Heating type	Product separation	Reactor Type	T (°C)/P(bar)/ residence time (min)	Ref.
Pacific Northwest National Laboratory, (PNNL) United States	1.5	Oil jacketed preheater Electric heat	Filter, blowdown pot, solids, separator, liquid collector, a back-pressure regulator Pressure regulating valve	CSTR + Tubular	(300–350)/200/ (27–50)	[43]
Aalborg University, Denmark	20	Hydrothermal pretreatment Two heaters	Two parallel high pressure filters, gravimetric separator Product barrel, pressure reduction Gravimetric separator	Tubular	(390–420)/ (300–350)/15	[46]
Chalmers University of Technology, Sweden	1	Preheater, electric heated jacket	Two pressure control valves installed in parallel	Fixed bed	370/250/(10–13)	[47]
The University of Sydney, Australia	15–90	Preheated in feed effluent exchangers	Back-pressure regulating valve	Coils in sand bath	(300–350)/ (120–200)/(3–5)	[48]
University of Illinois, USA	0.9–2.0	Heat Exchanger, electric furnace	Separation vessel, backpressure regulator, condenser	CSTR	305/103/(40–80)	[44]

Table 3
Benchmarking of HTL crude oil with refinery grade crude and transportation fuel.

Parameter	Microalgae [50]	Aspen wood [46]	Refinery Crude [55]	Diesel [55]
Viscosity, cP	15–500	–	10–100	1.1–3.5
Density, Kg/L	0.90–0.95	–	0.86	0.83
TAN, mg KOH/ gm Oil	20–40	–	<1	0
Ash, %	0.1 – 0.8	0.48	<0.1	0
Moisture, %	2 to 12	3.8	<0.05	0
Heating Value, MJ/Kg	35–38	34.3	41–43	45–46
S, wt%	0.2–0.5	0.3	0.5–2.5	15 ppm
N, wt%	4 to 7	0.5	0.1–0.75	10 ppm
H/C, Molar	1.5 – 1.7	1.3	1.5 – 1.9	1.79
O/C, Molar	0.015–0.15	0.15	0	0

FTICR-MS technique [51]. A range of heteroatom containing organic compounds, including species containing various nitrogenous and oxygen containing compounds with an extensive carbon number distributions, are typically present in the HTL crude bio-oil. Oxygenated compounds are usually formed when the lipids and carbohydrates molecules are broken in the HTL process whereas protein molecules are broken to yield several heterocyclic nitrogenous compounds (e.g. amides, pyrroles, pyridines, pyrazines etc.). The potential use of algal HTL crude bio-oil as feedstock for production of transportation fuel will require removal of these oxygenated and nitrogenated species to limit corrosion and instability during storage and emission of NOx compounds post combustion [57].

The crude bio-oil produced from HTL process from biomass feedstock is relatively similar to typical refinery crudes in characteristics. The same is represented in the boiling point curves of crude bio-oil which depict similar boiling ranges to refinery crudes. The main difference though is the presence of heteroatoms and small amount of inherent moisture and some ash, especially with algal feedstock. Upgradation of crude bio-oil (CBO) to usable transportation fuels is easier when compared to pyrolysis oil even with the same starting feedstock for both processes. This is very well represented by Van Krevelen diagram in Fig. 2. Typically, crude bio-oil fractions resemble as of weight fractions from slightly heavier crudes and have approx. 10–15% light + heavy naphtha fractions, 15–25% kero fraction, another 15–25% in diesel/ AGO range and rest (approx. 40–50%) in the range of VGO + Vacuum residue range.

The foremost question that arises typically with scale of process is the impact of the same on the quality of products as well as by-products. The seemingly imperceptible changes in the operating conditions can impact the consistency and quality of product in certain cases. Also, it is worthwhile to note the in larger systems tighter integration and control over the operating conditions might not be possible as is in the case of

laboratory trials. Keeping this in mind, we have done extensive studies for scale up of the HTL process from lab scale to bench scale continuous process and further from the bench scale to a large pilot scale facility for HTL. The key observations were that the quality of crude bio-oil showed no measurable change in the characteristics which were shown at all the three scales of testing and operation proving the effectiveness of the process and reliability of stable operation.

Upgradation of HTL crude bio-oil

High TAN number, moisture content, heteroatom content, lower heating value, and low H:C ratio are typically regarded as undesirable characteristics in any fuel and impact the direct application of crude bio-oil as transportation fuel [54,58]. Literature suggests that presence of water in certain quantity can enhance the overall quality by increasing stability, acid value and atomizing ability, and decreasing the viscosity and oxynitride emissions from the crude bio-oil [54,59]. However, higher moisture content can also result in lower calorific value of the oil. Crude bio-oil with high oxygen content is also known for its poor miscibility with refinery fuels. Moreover, crude bio-oil with high oxygen content has low stability at ambient conditions, which may lead to side-reactions during transportation and storage [54]. Therefore, crude bio-oil upgradation is necessary to address these drawbacks.

Various methods exist today for crude bio-oil upgradation, which include both physical as well as chemical methods like solvent addition, extraction, emulsification, hydrotreating, esterification etc. For example, ethanol and methanol, which are polar solvents, if added to the crude bio-oil reduce its viscosity and increase the calorific value as well [60]. Emulsification on the other hand is used typically to upgrade crude bio-oil to bio-diesel albeit at a higher cost [61]. Thus, it can be established that the addition of chemical can enhance the characteristics of crude bio-oils, but the key issue of high cost involved and difficulty in separation remain unsolved. Therefore, the present article mainly reviews other methods of upgradation such as hydrotreating, cracking, etc.

Hydro-processing is the process of treatment of organic/hydrocarbon feedstock in the presence of hydrogen, in the presence of catalyst. This helps in removal of heteroatoms as well as saturation of double and triple bonds. Hydrotreating and hydrocracking are two typical forms of hydro-processing techniques. Hydrotreating is a milder form of hydro-processing in which the feed undergoes saturation of carbon to carbon bonds and removal of heteroatoms [62]. Hydrotreating is essential in enhancing the quality of crude bio-oil, it improves the density, smoke points amongst other properties [63]. Hydrotreating being milder is also a cost-effective process to upgrade the crude bio-oil [62].

Hydrocracking is a combination of cracking and hydrogenation processes in presence of bi-functional catalyst. Hydrocracking is typically done in more severe operating conditions post hydrotreatment to avoid the deactivation of catalyst and helps in breaking the heavy molecules to produce lighter saturated hydrocarbon molecules.
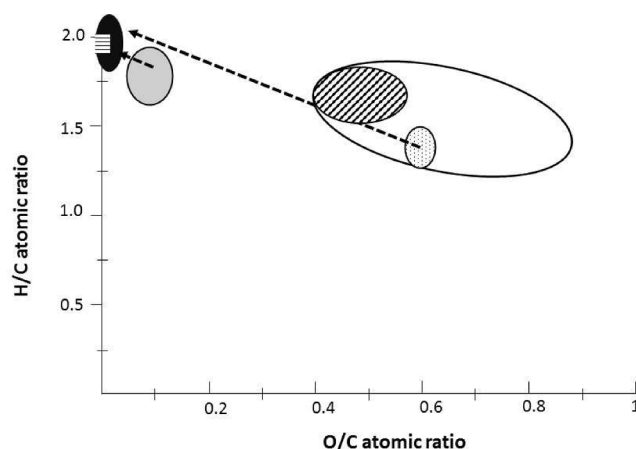
Fig. 2. Biomass & Bio-oil composition (Van Krevelene Diagram).

Keys: algae-⬤; biomass-◯; pyrolysis bio-oil-◌; HTL biocrude-⬤; fossile crude-⬤; Gasoline/diesel- ▤

Pre-processing of HTL crude bio-oil

Crude bio-oil from HTL of biomass provides a sustainable source for the production of chemicals and fuels. Crude bio-oil is more complex than typical refinery crudes, more so due to the presence of heteroatoms such are oxygen and nitrogen.

The heteroatoms can be removed in the upgradation section via hydrotreating or cracking or combination of both to yield pure hydrocarbon content, but the key challenge is to reduce the ash content along with the inherent moisture content in the crude bio-oil. To overcome this challenge, one simple solution would be to pre-process the crude bio-oil in the same way refinery crudes are pre-processed, i.e. in a desalter. A desalter can not only remove the moisture content but also removes the salts present in the crude bio-oil. Subjected to high temperatures in the range of 120–150 ^{0}C in the presence of a de-emulsifier along with the high applied voltage in the range of 3–5 kV, crude bio-oil can be easily separated from water along with the salts. According to the operating philosophy, the desalter can either be a standalone in case of bio-refinery or the crude bio-oil can be blended with refinery crude and processed in the typical refinery desalter. For very high salt contents of crude bio-oil which may be difficult to process as is in desalters, an option of upfront filter can also be explored to reduce the salt concentration of crude bio-oil.

Post processing of HTL crude bio-oil

Crude bio-oil is a highly viscous oil with relatively high heteroatom content along with heating value in the range of around 30–35 MJ-Kg^{-1}, depending on the type of feedstock. Maximizing the crude bio-oil yield requires optimum conditions which are specific and different for various kinds of feedstock. The produced crude bio-oil shows similar physical properties such as density and viscosity to those of heavy fossil crudes. The major difference is in the heteroatom (O/N) content, while sulfur content is relatively low with respect to heavy fossil crude. Hydrothermal Liquefaction of biomass with higher protein content typically produces crude bio-oil with high nitrogen content. The main nitrogen species are acid amides and heterocyclic aromatic compounds such as pyrroles, pyridines, pyrazines etc [64] and higher acidity is mainly due to free carboxylic acids in HTL crude bio-oil in case of algal feedstock.

Therefore, due to these factors, the produced crude bio-oil cannot be used directly as finished product or fuel due to heteroatom content, viscosity, high TAN and chemical instability. Thus, it requires post processing or upgradation of HTL crude bio-oil. The quality of crude bio-oil produced from HTL process significantly depends on the type of the feedstock that has been used and hence the upgradation requirement might also be different for different feedstock. Daniele et al. studied the hydrotreating of crude bio-oil obtained from three different feedstocks, namely, sewage sludge, lignocellulosic biomass and algal biomass using commercially available Ni-Mo/Al$_2$O$_3$ catalyst [65]. Sewage sludge crude bio-oil typically produced straight-chain hydrocarbons in the diesel range, with significant amount of heteroatoms removal even at mild hydrotreating conditions. Similar results were observed for algal crude bio-oil, although a key challenge for algal biocrude is the complete removal of the nitrogenous species. Upgraded crude bio-oil from lignocellulosic feedstock showed higher gasoline yields with higher aromatic content. Although effective and efficient removal of oxygen is possible, the nitrogen removal from the crude bio-oil is still a challenging task and is dependent on nitrogen containing compounds present in the crude bio-oil. Postprocessing of CBO can be done through various pathways (Fig. 3).

Standalone biorefinery

The first option is a standalone refinery or a bio-refinery, which can cater to the feed after it has been subjected to recovery of high value chemicals (HVC's). Crude bio-oil from several feedstocks can contain several high value bio-products such as long straight chain fatty, amides besides other compounds.

Configuration to maximize aviation turbine fuel (ATF) and diesel fractions

Fractional distillation of crude bio-oil from HTL yields fractions based on their relative volatility. These fractional cuts can then be processed further to get the desired high value products. Eboibi et al. investigated the vacuum distillation of algae derived crude bio-oil and reported that up to a max of 73 % of crude bio-oil could be distilled till the temperature of 360 ^{0}C compared to crude bio-oil obtained from a lignocellulosic feedstock. This primarily happens due to the relatively high lipid and protein content of algal feedstock [66]. Also, vacuum distillation greatly enhanced the quality of the crude bio-oil. Hoffmann et al. fractionated HTL crude bio-oil with approximately 53 % mass recovery at 375 ^{0}C, of which the equivalent gasoline, diesel and jet-fuel mass fractions comprised of 12.5%, 25.3% and 16.6 %, respectively [67]. In the approach of fractionation, oxygen gets distributed in all the distillation cuts and hence hydrotreating of the desired cut is only

required in the second stage post the fractionation of the cut.

Proposed configuration (Fig. 4) is optimized to maximize ATF and diesel with integrated residue cracking to maximize low boiling & high value products. The first step in this approach is fractionating the feed followed by hydro-processing the fractionated cuts. Hydro-processing is carried out in two steps: Hydrotreating (HT-1/HT-2) initially and thereafter Hydrocracking (HC). The lighter cut from the fractionation column, which primarily encompasses Kerosene range, is sent to HT-1 for hydrotreatment. After HT-1, the product falls in the category of ATF. The middle distillate is sent to HT-2 for hydrotreatment of cut which falls in the range of diesel. The bottom residue from fractionation is thereafter hydrocracked and distilled further to maximize ATF and diesel range fuel. The main advantage with this approach is primarily reducing the severity of hydro-processing by fractionation of cuts. The lighter cuts require lesser severity, and the heavier cuts are processed under higher severity. The two step hydrotreater produces ATF and diesel as the product cuts respectively. The key challenges with this configuration are high capex requirement for individual processing units of various fractionated cuts and the possibility of HT/HC catalyst poisoning due to high metal /salt content which is specific to particular feedstocks. Such issues can be overcome using either desalters or a guard bed upfront to prevent catalyst poisoning.

Overall, relatively higher CAPEX is expected compared to refinery integration option due to the requirement of standalone bio-refinery with its own unit operations. But the advantage of placing such bio-refineries even at remote locations may outweigh the transportation costs associated with refinery integration options in case the source of feedstock is far away from refineries.

Configuration to maximize gasoline and diesel fractions

The second configuration (Fig. 5) is optimized to maximize gasoline and diesel with integrated residue cracking to maximize low boiling & high value products. Heteroatom removal in the first step itself smoothens downstream processing while lower grade MOC of downstream equipment becomes feasible due to low total acid number (TAN) or carboxylic acid number (CAN). The primary steps are upfront hydrotreatment followed by fractionation. The first stage hydrotreatment ensure the removal of heteroatoms which may pose issues for downstream equipment. Thereafter, the hydrotreated feed is fractionated in two steps to maximize the yield of gasoline and diesel. After that, the

residue is again hydro-cracked and fractionated to get the distilled products. This particular approach maximized the yield of transport fuels from HTL crude bio-oil.

The key challenge in the process is again the requirement of high capital expenditure (CAPEX) as explained earlier due to a standalone bio-refinery. Another requirement in such a configuration may be the need of ash removal upfront in case of feedstocks which yield oil with higher ash content to prevent the poisoning of catalyst in the hydrotreater section. This can be easily achieved with a de-salter configuration upfront of the hydrotreatment section.

Refinery integration of HTL facility

The second option is integration with an existing refinery, with two key integration strategies. The first strategy is blending of HTL crude bio-oil with fossil crude and the second is blending with hydrotreated vacuum gas oil (VGO) for fluid catalytic cracking (FCC) reactor.

Blending of HTL crude bio-oil with fossil crude

The major benefits of refinery integration shall always be the minimal requirement of CAPEX for upgradation of the crude bio-oil produced from HTL. The first pathway is blending with fossil crude, as CBO exhibits relatively similar properties to crude which makes the co-processing possible (Fig. 6). The blended crude can then easily be sent to the downstream equipment i.e. desalter, for processing of the same. Besides saving CAPEX, the option also has the advantage of supplementing the requirement of crude of any refinery along with making the process more sustainable and renewable.

The fractions of crude bio-oil have been observed to be in the same range as of typical heavy crudes and hence can be easily blended and processed in any refinery which can handle such crudes, in the required blends. One of the key issues is the presence of ash and water in crude bio-oil, specifically for the feedstocks such as salt-water algae, which may be the limiting factor in determining the percentage blend feasible for such crude bio-oils. Although, with major refineries operating at huge throughputs, the blending at a certain percentage should not be an issue.

Blending of HTL crude bio-oil with FCC feed

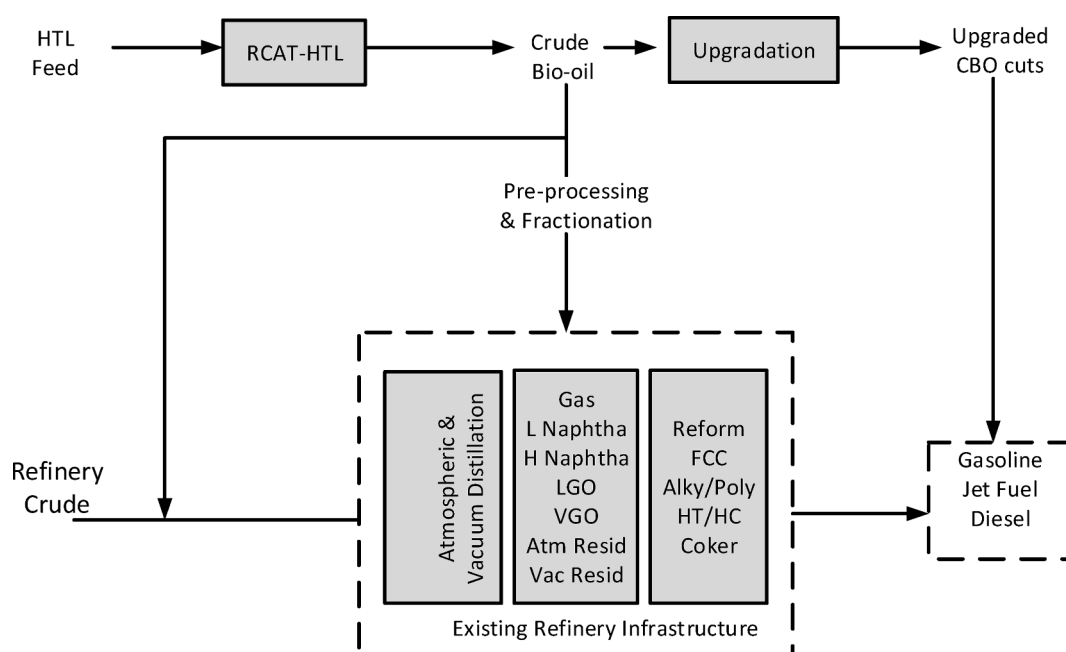Catalytic cracking can remove heteroatoms such as oxygen along

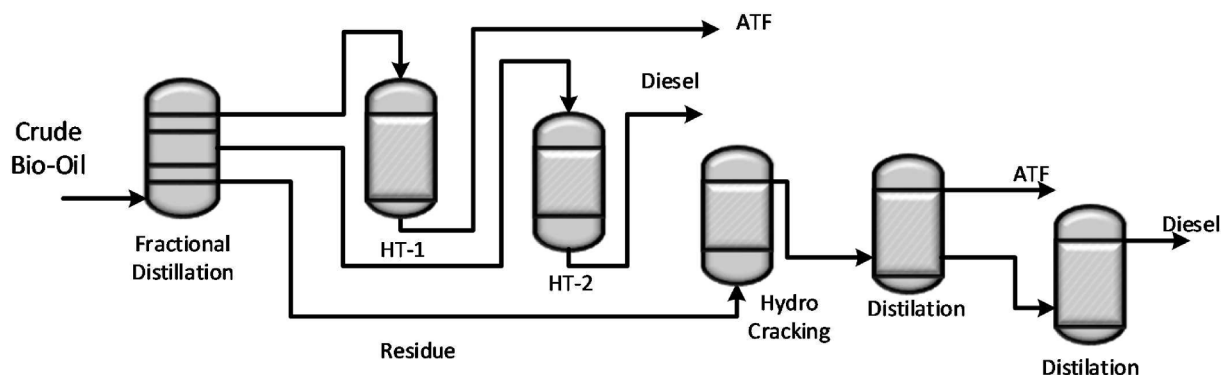**Fig. 3.** Various pathways to depict the upgradation route of crude bio-oil.

Fig. 4. Configuration to maximize ATF and diesel fractions.
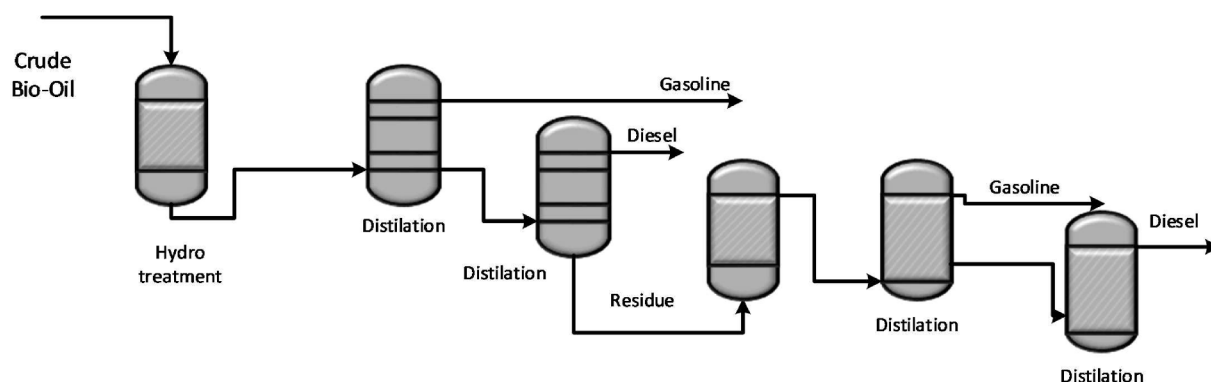

Fig. 5. Configuration to maximize gasoline and diesel fractions.

with the moisture content and facilitates the esterification of alcohol and acidic compounds in crude bio-oil [54]. These cracking reactions also reduce the viscosity and TAN of crude bio-oil. The primary goal of catalytic cracking is improving the yield and quality the feedstock that is being processed. This process can typically be conducted in a fixed-bed or fluidized-bed reactor system in the presence of acid catalysts (zeolites and silica-alumina) [54,68].

The second pathway (Fig. 7) blends crude bio-oil with FCC feed, which is hydrotreated VGO. Key advantage again in the scheme is that no additional CAPEX would be required, and FCC can easily handle feeds of this quality. Sweet VGO from the hydrotreater can be easily blended with the crude bio-oil from HTL plant. The blended feed can then be directly sent to the FCC reactor to be processed. The feed flexibility of the FCC reactor comes in handy to process such blends. Depending on the type of feedstock being used for HTL operation, pre-determined ranges can be set for the blending of crude bio-oil in sweet VGO based on the blends operating parameters and process requirements such as the metal content etc. For crude bio-oil with higher amount of ash/metal content specific to particular feedstocks such as salt-water algae, an upfront requirement to desalt the oil may be required to prevent the catalyst poisoning of FCC reactor.

Merits and demerits of the upgradation strategies and their current status

As discussed earlier, the key implications with standalone bio-refineries for HTL crude bio-oil upgradation will be primarily related to the CAPEX requirement. Besides that, such installations will also require an upfront desalter to remove the ash and moisture content to prevent the de-activation of hydro-processing catalyst. Other major issue can be the high TAN values which may cause the corrosion of internals of such bio-refineries. Of course, the TAN, ash and moisture parts are confined to a few feedstock only such as MSW, algae etc, but the CAPEX part would be a point in case on any feedstock. On the other
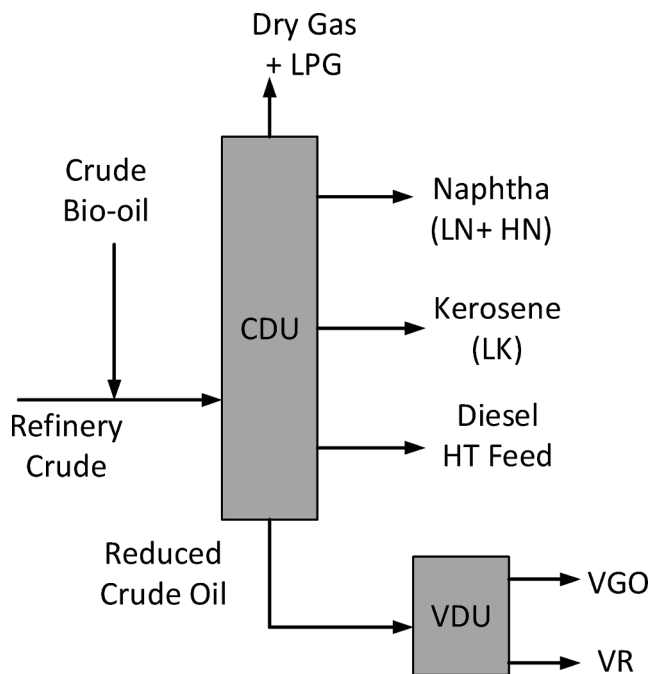

Fig. 6. Blending of CBO in the feed of crude distillation unit.

hand, a standalone bio-refinery also removes the dependency on an existing refinery nearby and can be tuned to specific needs of the end user.

The option of refinery integration stands on the other end of horizon. It has the obvious advantage of negligible CAPEX requirement, along

with a host of options for inserting the crude bio-oil and/or its fractions into the refinery. The lower cost makes it an attractive option. Few issues pertaining to ash, moisture content, TAN etc. can easily be dealt with due to the option of deciding the blend ratio appropriately based on unit specifications. Albeit, in case of refinery being far away from the production site, the cost of transportation may be prohibitive and having a nearby refinery becomes an integral requirement of this particular option.

Currently large-scale upgradation scheme and operations have not been explored globally primarily due to the reason of smaller capacity of HTL units. Reliance has not only produced a large quantity of crude bio-oil over several years of operation but also has tested out majority of the listed options successfully at pilot continuous units, be it hydrotreating, hydrocracking, blending with various refinery feeds/products, FCC operation etc.

HTL by-product treatment and utilization

HTL is one of the most promising technology for the production of bio-fuels via the route of thermo-chemical processing. The major products and by-products generated from the process include biocrude, nutrient rich process water which has several organic constituents, phosphorus rich solids and gas containing CO_2, methane etc [69]. One of the challenges which is associated with the HTL process is the presence of large quantity of organic carbon in the aqueous/water phase, which effectively represents the lower carbon efficiency in terms of carbon fixed in crude bio-oil. Researched have proposed several processes to cater this issue, one of which is catalytic gasification of the aqueous phase to produce syngas while reducing TOC of the aqueous [70]. Catalytic hydrothermal gasification (CHG) is one such process which can be used to produce fuel gas and hydrogen [71]. At high temperatures and pressure and in presence of a catalyst, CHG converts the organic portion of the aqueous in to CH_4, H_2 CO_2 and CO [72]. Zhu et al. conducted an economic analysis for an algae HTL and crude bio-oil upgrading system with alternative aqueous phase treatment methods [73]. Three different methods were distinctly compared: 1) direct recycle of HTL aqueous phase to algal ponds 2) Catalytic Hydrothermal Gasification (CHG), and 3) Anaerobic Digestion (AD). Direct recycle has the obvious advantage of lowest cost associated with it, due to the requirement of just pumps and buffer tanks for storage and supply, while CHG and AD both have extensive CAPEX requirement along with higher operating costs as well, which increases the minimum fuel selling price (MFSP) over the direct recycle case by 11% and 2.9%, respectively. The CHG and AD routes also increase the conversion cost (excludes the cost to grow, harvest, and dewater algae) by 75% and 21% respectively.

The aqueous recycle route has other advantages as well. Besides lowering the water requirement of the end to end process, it also recycle nutrients such as N, P and reduces the demand/cost of the same [74]. Biller et al. conducted HTL of distiller's grain with and without catalyst (K_2CO_3) by recycling HTL aqueous phase to the reactor [75]. Both the catalytic and non-catalytic cases depicted a significant improvement in crude bio-oil yields from approximately 35 to 55 wt% with an increase in energy recovery of up to 95%. Yulin et al. conducted similar HTL experiments using Chlorella vulgaris, again with and without catalyst by recycling the HTL aqueous phase to the reactor and depicted and increased oil yield compared to the base catalytic HTL case [76]. Patel et al. compared HTL aqueous phase recycle with energy generation via AD process and projected that the recycling case has slightly better environmental benefits even when compared to the AD process [77].

The HTL aqueous phase typically has all the required nutrients for algal growth. The trials with the recycled HTL aqueous show that several compounds present in it such as phenols, fatty acids and nickel can lead to inhibition in the productivity of algae thereby necessitating dilution. For various strains of algae, different optimum dilutions were observed
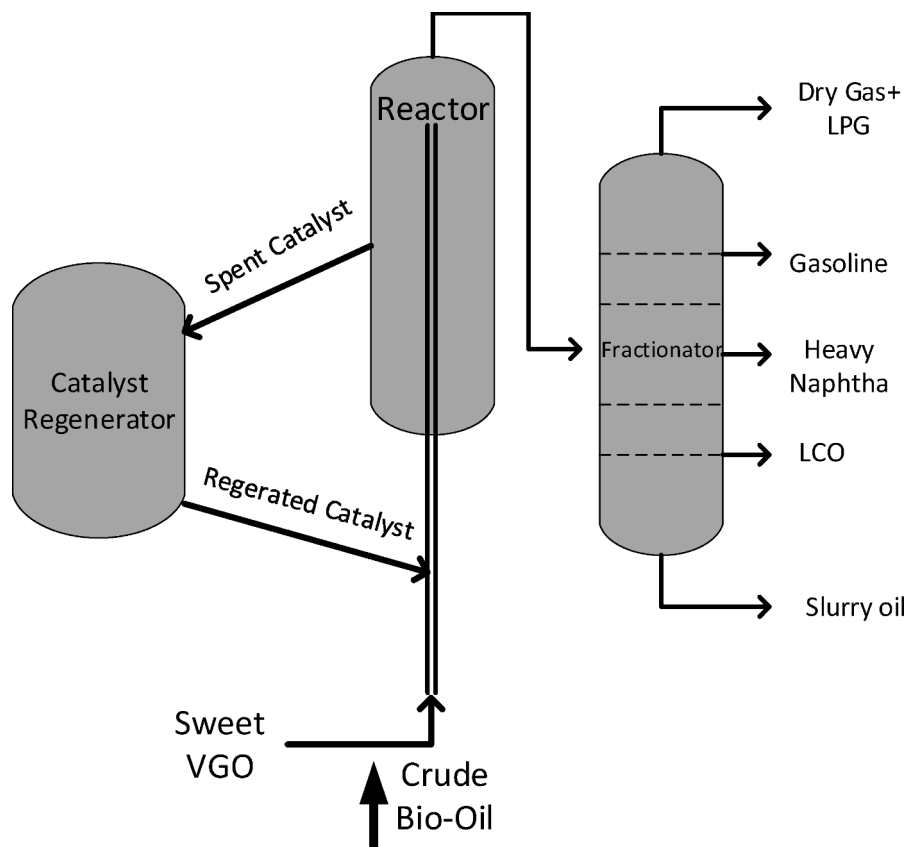

Fig. 7. Blending of CBO with FCC feed.

[78]. Emundsen et al. conducted algal cultivation with recycled phosphorus from solid residue and nitrogen from the aqueous phase [79]. The highest productivity rates of both Scenedesmus and Chlorella sorokiniana were equivalent to growth rates observed in the control medium using standard lab grade potassium phosphate salts. Although, as mentioned previously, inhibitory compounds present on the aqueous phase certainly make the uptake of nitrogen a bit difficult. Cheng et al. observed the presence of adverse reaction between protein aqueous and Lignin inhibiting the generation of crude bio-oil [80]. More studies are needed to evaluate the recycling of aqueous phase in terms of pH changes, metal accumulation and the impact on crude bio-oil quality before introducing such recycle in larger continuous scale systems. Even then, only a certain percentage of the HTL aqueous phase can be recycled to maintain favorable biomass to solvent ratio. Therefore, a continuous large scale HTL process will likely face the key issue of wastewater disposal [79].

For HTL of other feedstock such as MSW, food waste, refinery sludge, vegetable waste etc., the option of aqueous recycle to ponds is not viable. For such cases, the option of HTL aqueous recycle to the feed of the HTL process can be explored. This can be achieved by mixing the HTL aqueous from product separation section with the HTL feed which is sent to the pre-treatment section. The key benefits associated with recycling the aqueous phase are 1) Enhancement of crude bio-oil yield due to conversion of recycled organics 2) Lower fresh water requirement for the preparation of feed/slurry 3) The aqueous acts as a solvent, especially for dry lignin based feedstock thereby enhancing the homogeneity of the slurry 4) Value creation from aqueous phase. The key challenges that may be associated with recycling the aqueous phase are: 1) To prevent build-up of salts, mineral and heteroatoms, a bleed stream will be required 2) To achieve desired solid loading in HTL feed, only a part of HTL aqueous can be recycled, therefore the remaining portion of aqueous will still need further treatment. The recycling can also be achieved by upfront treatment of HTL aqueous through membrane separation techniques to recover organics for recycle and produce industrial grade water. However, this method involves additional CAPEX and OPEX.

Future research recommendations and final perspective

The key areas of improvement which still need further research are the following

a) Pretreatment of Feed – Upfront removal of inorganic components such as ash, salt, minerals/inert will help not feed processing but will also improve the quality of crude bio-oil as other by products

b) Heat Exchanger – Further research is required to suppress charring issues in the exchanger, particularly in the region of 150–300 °C. Also, significant improvement may be needed in the design and cleaning philosophy of the exchangers to minimize the downtime of the exchangers.

c) Reaction section – Optimization of process conditions for maximizing the crude bio-oil yield, including optimization of catalyst and reaction conditions, such as residence time, solid loading and temperature. Scaled up solid separation scheme to separate bio-char with minimized process interruption will be required for further optimization of the process.

d) Upgradation of crude bio-oil – Optimization of the unit operations such as desalter and hydroprocessing units will be necessary as these unit are typically designed and operated for fossil crudes and their fractions. Also, typical commercial catalysts might not be the most efficient for crude bio-oils which have significant amount of heteroatoms such as Nitrogen and Oxygen present in them.

The critical engineering challenges associated with the scaling up and commercialization of the HTL process were reviewed in detail and highlighted in this work. The article also aims to summarize different solutions that are explored in various literature studies. Some of the prevalent issues and challenges observed in various experimental research work on development of a continuous HTL process are: designing a flexible pretreatment section for various biomass types to produce homogenous and pumpable slurry, selection of high pressure pump type, fouling and charring in heat exchangers, HTL reactor design to maximize yield and overall reaction performance, separation techniques for solid removal including salts/ash in HTL reaction products and crude bio-oil processing and upgradation methods.

Feedstock type, compositional variation and rheological properties demand an optimized feed processing scheme to generate desired range of particle size and slurry concentration. Literature studies have reported large variation in the slurry behavior when it is heated and subjected to shear stress. Positive displacement pumps are most commonly utilized for developing high pressure required in HTL process. Multiple stage pumping options are frequently used. However, pumps are prone to operational challenges such as pressure fluctuation, clogging and leakages caused due to mechanical failures. Many biomass slurries are complex unconventional feeds and limited data on thermophysical properties is available in literature. Some of the slurries are found to be highly viscous and charring in nature. Therefore, designing of conventional heat exchangers for biomass applications has proven to be difficult. Several types of heat exchangers such as shell & tube, spiral, and double pipe exchangers are discussed in this work. Key parameters affecting the selection and design are viscosity, specific heat, fluid velocity, and fouling factor. Heat integration is desired at commercial scale to minimize the overall process duty and support favorable economics. Importance of skin temperature and gradient on charring and fouling of tubes is also highlighted in studies.

Biomass composition also plays a very critical role in design of the HTL reaction section. Understanding the reaction mechanism helps immensely to optimize the process conditions such as temperature and residence time. Lot of HTL research work is carried out in batch reactors. Though these studies are quite beneficial in studying the reaction conditions, product yield and characteristics, they have limited applications for commercial scale. Continuous flow reactors provide flexibility with controllable residence time to maximize crude bio-oil yield. Energy integration can be effectively realized in a continuous configuration process. The most common reactor configuration reported in studies is tubular, which benefits from ease of scalability and absence of moving parts. However, stirred reactors or combinations of stirred and plug flow reactors are also documented. Stirred reactors can have the great advantage of reducing plugging and allowing faster heat exchange. Nevertheless, heat transfer can be also increased in tubular reactors by utilizing an oscillating flow as highlighted in some studies. For most of the current HTL continuous processes, residence times between 15 and 30 min are adopted. Product separation technique of reaction effluent stream is an important design aspect of a HTL reactor. Presence of solids and elevated process conditions makes it difficult to separate out solids and cause plugging issues. Formation of Pickering emulsion due to fine solid particles is likely to form near the inlet of the back-pressure regulator and products collection system; hence solids separation upstream in the region of high temperature and high pressure is advised. Other potential solutions suggested to solve the clogging problem are minimizing reaction time, reducing ash content, increasing tube diameter and increase the slurry pumpability.

Even though crude bio-oil has a lot of similar properties when compared with typical fossil crude, the key challenges in the post processing of crude bio-oil are the high heteroatoms content(O&N), moisture, ash and TAN content. These issues are invariably dependant on the type of feedstock used and several measures have been reported in the manuscript to overcome these challenges and finalize the upgradation strategy. Ash and water content can be handled by installing a desalter unit and heteroatom content can be targeted by the HT/HC units. Acids and other HVC's can be extracted and thereafter crude bio-oil can be processed in the upgradation pathways which maximizes the desired

products. The two key pathways discussed are standalone bio-refinery and integration with existing fossil crude refineries. The bio-refinery path can be tuned to maximize either gasoline and diesel or ATF and diesel whereas the refinery integration points can be either blending with crude at the upfront of crude oil distillation unit (CDU) or a blend with sweet VGO prior to sending it to FCC unit.

CRediT authorship contribution statement

Rajaram Ghadge: Conceptualition, Investigation, Methodology, Writing – review & editing. **Nitin Nagwani:** Writing – original draft, Data curation, Formal analysis. **Nikhlesh Saxena:** Writing –original draft, Data curation, Formal analysis. **Santanu Dasgupta:** Project administration, Supervision. **Ajit Sapre:** Project adminstration, Supervision

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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