

ECONOMIC AND EUROPEAN UNION ENVIRONMENTAL SUSTAINABILITY CRITERIA ASSESSMENT OF BIO-OIL BASED BIOFUEL SYSTEMS: REFINERY INTEGRATION CASES

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ABSTRACT: The biofuel mix in transport in the UK must be increased from currently exploited 3.33% to the EU target mix of 10% by 2020. Under the face of this huge challenge, the most viable way forward is to process infrastructure-compatible intermediate, such as bio-oil from fast pyrolysis of lignocellulosic biomass, into biofuels. New facilities may integrate multiple distributed pyrolysis units producing bio-oil from locally available biomass and centralised biofuel production platforms, such as methanol or Fischer-Tropsch liquid synthesis utilising syngas derived from gasification of bio-oil. Alternative to bio-oil gasification is hydrotreating and hydrocracking (upgrading) of bio-oil into stable oil with reduced oxygen content. The stable oil can then be co-processed into targeted transportation fuel mix within refinery in exchange of refinery hydrogen to the upgrader. This paper focuses on the evaluation of economic and environmental sustainability of industrial scale biofuel production systems from bio-oils. An overview of bio-oil gasification based system evaluation is presented, whilst comprehensive process reaction modelling (with 40 overall bio-oil hydrocracking and hydrotreating reaction steps), simulation, integration and value analysis frameworks are illustrated for bio-oil upgrading and refinery co-processing systems. The environmental analysis shows that the former technologies are able to meet the minimum greenhouse gas (GHG) emission reduction target of 60%, to be eligible for the European Union (EU) Directive's 2020 target of 10% renewable energy in transport, whilst at least 20% renewable energy mix from an upgrader is required for meeting the EU GHG emission reduction target.

Increases in the price of biodiesel and hydrogen make co-processing of stable oils from bio-oil upgrader using refinery facilities economically more favourable than final biofuel blending from refineries and create win-win economic scenarios between the bio-oil upgrader and the refinery. The range of the cost of production (COP) of stable oil (328 MW or 0.424 t/t bio-oil), steam (49.5 MW or 0.926 t/t bio-oil) and off-gas or fuel gas (72.3 MW or 0.142 t/t bio-oil) from a bio-oil (LHV of 23.3 MJ/kg) upgrader process is

evaluated based on individual product energy values and global warming potential (GWP) impacts. The minimum and the maximum annualised capital charge predicted by the Discounted Cash Flow (DCF) analysis correspond to 25 operating years and 10% IRR; and 10 operating years and 20% IRR; respectively. Based on this DCF strategy and 1200 \$/t of hydrogen and 540 \$/t of biodiesel market prices, the selling prices of 259.32 \$/t, 34.85 \$/t and 174.27 \$/t of the stable oil, steam and fuel gas, respectively, from the upgrader to the refinery were obtained to create win-win marginal incentive for the upgrader and refinery systems, individually. If stable oil from a bio-oil upgrader can be launched as a product potentially to be used in refinery hydrocracker (at a competitive price of 490 \$/t), for the production of renewable diesel, upgrader can be operated independently, such as, purchase hydrogen from vendors at competitive price, with comparative marginal incentives. The bio-oil upgraders, either stand-alone or integrated, were designed to meet desired product specifications, diesel with specific gravity: 0.825 and cetane number: 57 and stable oil with API: 30.1 and cetane number: 28.7, for co-processing through the refinery hydrocracker, respectively.

Keywords: biomass pyrolysis, methanol synthesis, Fischer-Tropsch, bio-oil upgrader, hydroprocessing, biorefinery utility systems

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1. INTRODUCTION

The production of biofuel needs to be seriously considered to reduce our reliance on petroleum. As a result of oil spill in the Gulf of Mexico in 2010, the moratorium is forecasted to last for several years affecting the world oil production significantly. The UK's biofuel supply accounted for 3.33% of the total road transport fuel in the past year that exceeded the Government's target of 3.25%¹. However, there is a need for significant increase in the production of biofuel by 2020. The EU target for biofuels is to account for 10 percent of all automotive fuel consumption by energy content by 2020². The EU Renewable Energy Directive emphasises on sustainability criteria in biofuel development. The Directive further stipulates that only biofuel systems that achieve GHG emission savings of 60% will be eligible to be considered for the 2020 target of 10% renewable energy in transport². While the policies can influence the biofuel proportion in the transportation fuels, the decision is on the prioritisation of biofuel technology investment to meet 2020 target.

It is challenging to widely exploit biofuel production technologies, from their current status of biodiesel production from oily crops, bioethanol from sugar based crops and ethyl tertiary butyl ether from bioethanol, to the development of lignocellulosic biorefinery, based on agricultural and forestry wastes and residues, etc. The technological and economic feasibility and environmental sustainability of the new generation biorefineries must be assured. Systems analysis tools enable highly complex, flexible and efficient polygeneration processes and shared infrastructures, preservation of natural resources and minimisation of environmental impact and waste disposal. Contributions include process synthesis, integration and systematic hierarchical design tools for biorefineries and for pollution and GHG emission control³⁻⁴, computer-aided process engineering tools for systematic analysis of product and process design and sustainable development⁵⁻⁶, optimal biorefinery product allocation by systematic modelling of processes, economic potential and environmental impact⁷, systems platform for optimal synthesis of biomass based manufacturing processes⁸⁻⁹ and applications of process and supply chain optimisation¹⁰. Nevertheless, the systems analysis tools are under deployed in biorefinery design and decision making on prioritisation of process innovations and investments. This work attempts in developing a strategy with

coherent and coordinated activities in order to enable techno-economic and environmental sustainability analyses of bio-oil based biorefinery process design alternatives, generating useful information for policy directives and for the prioritisation of process investment and innovation (Fig. 1). The bio-oil based biorefinery process simulation and integration frameworks were deployed for economic value analysis in terms of the Cost of Production (COP) of products and environmental sustainability analysis in terms of the Greenhouse Gas (GHG) emission reduction potential (Fig. 1). The COP of a stream includes various cost elements, such as the cost of raw materials, operating cost and capital charge associated with the production of the stream¹¹⁻¹⁶. The GHG emission accounting includes global warming impacts from all Greenhouse Gases to the atmosphere in terms of equivalent CO₂ emissions per unit amount of energy produced (or per equivalent mass).

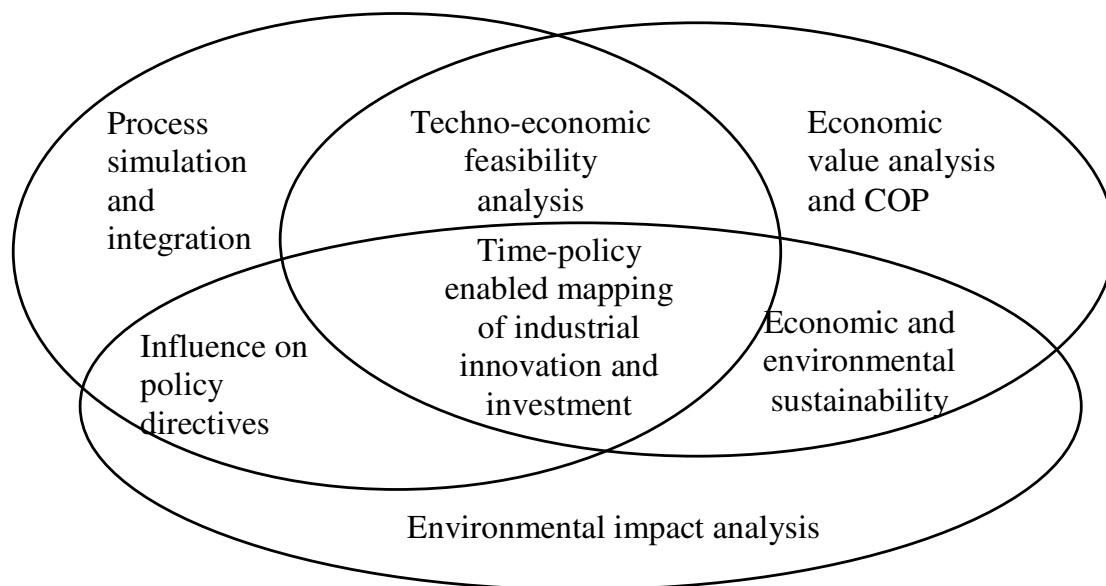


Figure 1. Process simulation, integration and analysis framework

With rapidly growing interest in the development of flexible biomass pyrolysis process, pyrolysis oil or bio-oil can become a promising infrastructure-compatible intermediate to establish biofuels¹⁷⁻¹⁹. A number of significant advantages exist in fast pyrolysis as a pretreatment step for converting biomass into liquids, ~8-12 times more bulk density; removal of char along with alkali metals; lower tar content; ease and lower cost in handling, storing and transporting liquids to the production as well as reception sites¹⁸. These advantages have led to the concept of integration between decentralised small scale pyrolysers

utilising locally available biomass and centralised biofuel production plant. Promising routes in a centralised plant may constitute of bio-oil gasification followed by Fischer-Tropsch (FT) liquids (alternatively methanol synthesis)^{18, 20}; and mild hydrotreating to severe hydrocracking of bio-oils into gasoline and diesel products (upgrader) (Fig. 2). The economic feasibility of energy and capital intensive upgrader processes can be enhanced by integration with other industrial facilities, including gasification route itself, refinery (focus of this study), chemical and pulp and paper industry.

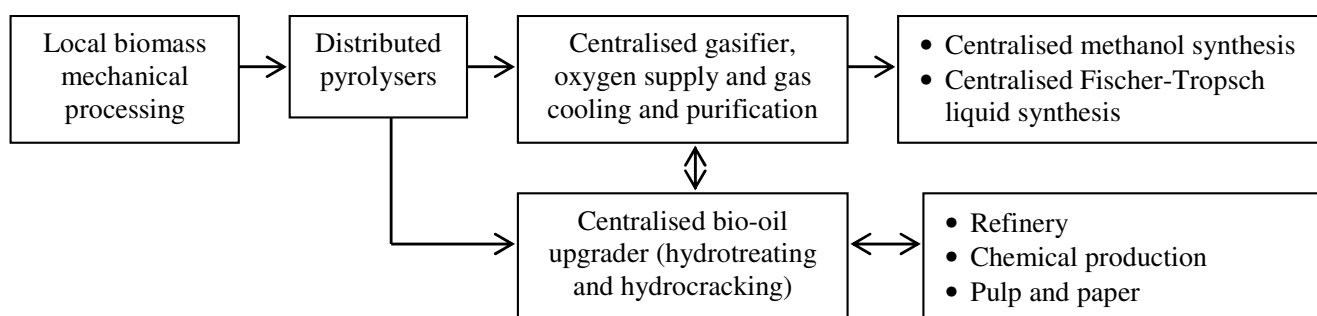


Figure 2. Integrated decentralised local biomass pyrolysers and centralised biofuel production plants

This study includes the GHG emission saving analysis of industrial scale bio-oil gasification based systems in the context of 60% GHG emission saving requirement for eligibility to be considered for the 2020 target of 10% renewable energy in transport by the EU Renewable Energy Directive, 2009², in order to complement the up-to-date published works on the techno-economic analysis of thermochemical biomass systems¹⁷⁻²⁰. Additionally, to date only a few studies on bio-oil upgrading via hydroprocessing, hydrotreating and hydrocracking to diesel and gasoline have been reported²¹⁻²⁵. These studies have reported techno-economic feasibility analysis of transforming biomass into hydrocarbon fuels such as gasoline and diesel, through a series of biomass pyrolysis process and hydroprocessing routes. They discussed about the deployment of catalytic hydroprocessing of bio-oil into fuels, including the application of a range of tested catalysts and various processing routes and conditions. Economic sensitivity analysis associated with co-locating the plant with existing refinery has also been performed. However, the above studies do not provide proprietary information on hydroprocessing reaction mechanisms²¹⁻²⁵. Thus, the implications of reaction conversion and severity on product compositions and blending properties are not clearly understood. None of these studies was either concerned about the EU

sustainability criteria assessment² and thereby prioritisation of the bio-oil upgrader investments. This work takes the above scopes as an aim to develop comprehensive and transparent process reaction model with 40 overall bio-oil hydroprocessing reaction steps and simulation and integration frameworks for the evaluation of blending properties, economic values and GHG emission saving potential of bio-oil upgrader systems. Hundreds of elementary reactions may occur simultaneously in a hydrocracker or hydrotreater process. At the least, fewer, but adequately representative overall reaction steps, such as cracking to olefins and hydrogenation to high octane isoparaffins (mainly in gasoline), ring separation and opening into smaller aromatic compounds and cycloparaffin (mainly in diesel) and side chain hydrocracking and isomerisation²⁶ should be hypothesised in order to have better control over upgrader product and process performance. Alongside, refinery co-processing system economics were analysed with a more practical objective of creating win-win economic scenarios between the two systems.

2. GHG EMISSION SAVING ANALYSIS OF GASIFICATION BASED SYSTEMS

Between bio-oil gasification and upgrading routes in Fig. 2, the former route comprises of proven technologies and “can be commercially deployable by industrial companies with infrastructure and expertise available to produce marketable products”¹⁸. A key technological barrier is the adaptation to different commercial scale operations according to the quality, availability, transportation and delivery requirement of biomass resource. Table 1 presents an overview of industrial process specifications, gasification²⁷, air separation unit for supplying oxygen for the gasifier²⁸, methanol synthesis²⁹, FT liquid synthesis reactor³⁰ and hydrocracker²⁶. Pyrolysers with biomass processing capacities of 96 t/d^{18, 31}, 490-550 t/d^{32, 33} and 1001 t/d³⁴ can be implemented for distributed generations of bio-oil.

Table 1. Overview of major process units, technology developers and capacities

Process Unit	Technology Developer	Capacity for single unit
Gasifier	Shell, GE, E-Gas, Koppers Totzek, Destec, Prenflo.	up to 2000 t/d of coal ²⁷
Cryogenic ASU	Air Products, Universal Industrial Gases, etc.	90-820 t/d of oxygen ²⁸
Methanol synthesis reactor	Lurgi, ICI, Air Products, etc.	5000 t/d of methanol ²⁹
FT synthesis	Shell (SMDS), Sasol (ARGE), etc.	~6000 bbl/d of FT

reactor		products ³⁰
Hydrocracker	UOP, Exxon, Shell, etc.	35 kbb/d of feed ²⁶

Fig. 3 illustrates mass and energy balance across a distributed pyrolysis plant, based on large scale pyrolysis process studies, by NREL³². Woody resources, such as short rotation coppice have been studied widely and thus used as a test case to establish the various concepts in this paper. It is estimated that 25-125 distributed plants based on 1 kt/d and 0.2 kt/d pyrolysis capacities respectively may be required to convert a total of 25.3 kt/d of biomass into 16.7 kt/d of bio-oil. 8-9 trains entrained flow gasifier unit would process these bio-oils into gas, which can then be processed through a methanol synthesis unit, to produce 5.5 kt/d of methanol, in a centralised plant. Alongside, low grade heat and electricity are produced, 8% and 3% of the total energy output, respectively. An energy efficiency of 61.5% from a centralised bio-oil to methanol production plant is obtained, based on bio-oil LHV of 23.3 MJ/kg and methanol LHV 20 MJ/kg, respectively. In a centralised bio-oil based FT liquid synthesis plant, the FT liquid, heat and electricity contribute to 54%, 33% and 13% of the output energy from the centralised plant, operating at 58% efficiency, based on the given LHV of bio-oil. The mass and energy balance obtained from process simulation of bio-oil based centralised plants detailed elsewhere²⁰, is presented in Fig. 4.

Fig. 4.

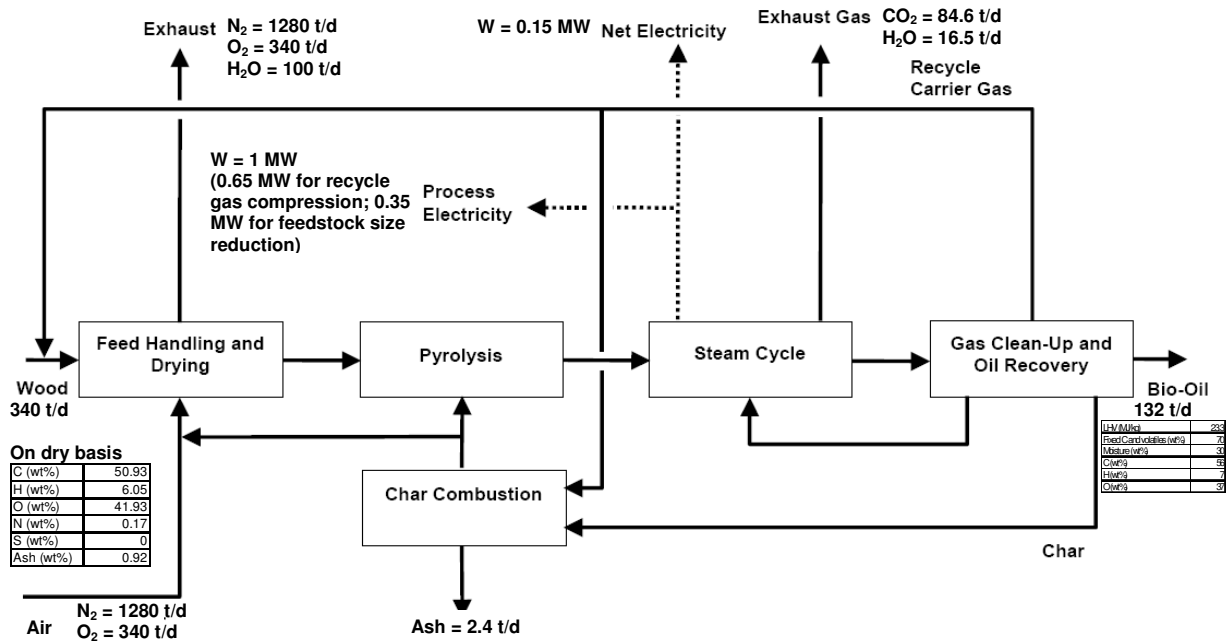


Figure 3. Mass and energy balance across distributed pyrolysis plant

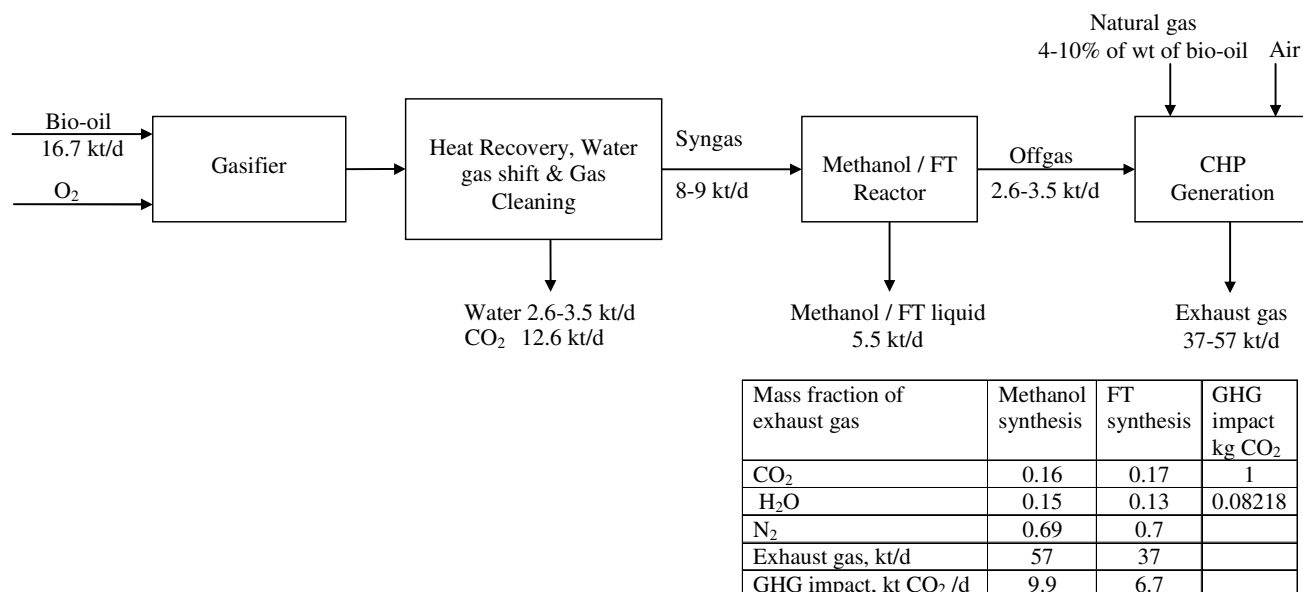


Figure 4. Mass and energy balance across centralised methanol and FT liquid synthesis plants

GWP Impact: The GWP impacts from the operations of distributed biomass based bio-oil production plant (Fig. 3) and centralised bio-oil processing plant for the synthesis of methanol or FT liquid (Fig. 4) and from the combustion of end product are predicted. The GWP impact per unit mass of end product from overall plant operations (Figs. 3 and 4) and combustion by taking account of the corresponding plant yields is illustrated for methanol synthesis in Eq. (1). The mass balance and plant yield parameters for determining the GWP impact under various system boundaries are discussed as follows.

Emission from distributed biomass based bio-oil production plant: The quantities of GHGs, CO₂ and H₂O, emitted from a distributed pyrolysis site are 84.6 t/d (in the exhaust gas from the steam cycle in Fig. 3) and 116.4 t/d (100 t/d of water vapour emitted with the exhaust gas from the feed handling and drying and rest from the steam cycle in Fig. 3), totalling to 94.2 t/d of CO₂ equivalent GWP (**0.28 kg CO₂ / kg of biomass in Eq. 1**). Note that the input biomass, 340 t/d of wood, to the pyrolysis site in Fig. 3 includes 100 t/d of moisture content in it, whilst wood ultimate analysis is provided on dry basis. Steam is assumed to contribute to GWP by 0.08218 kg CO₂ equivalent³⁵.

Emission from centralised bio-oil processing plant: In both the methanol and FT liquid synthesis centralised plants, a portion of CO₂, 0.75 kg/kg of bio-oil separated by Sulfinol unit (from the ‘Heat recovery, water gas shift and gas cleaning block’ in Fig. 4) is capture-ready and therefore, is not

accounted in the plant GWP impact. CO₂ along with water vapour and nitrogen (in air) in the exhaust gas is emitted to the atmosphere after CHP generation. The mass fractions and flowrates of the exhaust gases from the methanol and FT liquid synthesis centralised plants are indicated in Fig. 4. CO₂ and water vapour contribute to the GWP by a total of 9.9 kt CO₂ / d (= (0.16 + 0.15×0.08218) × 57) or **0.6 kg CO₂ / kg of bio-oil in Eq. 1** and 6.7 kt CO₂ / d (0.4 kg CO₂ / kg of bio-oil) from methanol and FT synthesis centralised plants, respectively (Fig. 4).

Emission from bio-methanol combustion: The GHG emission from the combustion of 5.5 kt/d of methanol (Fig. 4) (or 0.33 kg of methanol / kg of bio-oil) is 8.1 kt CO₂ equivalent / d (**0.48 kg CO₂ / kg of bio-oil in Eq. 1**). Hence, the GWP resulting from the operation of distributed bio-oil production plant, centralised bio-oil processing plant (into methanol and CHP) and from the combustion of methanol is 2.18, 1.8 and 1.47 kg CO₂ / kg of methanol, respectively (Eq. 1).

$$\begin{aligned}
 & \text{GWP impact from pyrolyser, kg CO}_2 \text{ / kg of methanol} \\
 & = 0.28 \frac{\text{kgCO}_2}{\text{kgBiomass}} \times \frac{340 \text{ kgBiomass}}{132 \text{ kgBio-oil}} (\text{Figure3}) \times \frac{16.7 \text{ kgBio-oil}}{5.5 \text{ kgMethanol}} (\text{Figure4}) \\
 & = 2.18 \\
 & \text{GWP impact from centralised platform, kg CO}_2 \text{ / kg methanol} \\
 & = 0.6 \frac{\text{kgCO}_2}{\text{kgBio-oil}} \times \frac{16.7 \text{ kgBio-oil}}{5.5 \text{ kgMethanol}} (\text{Figure4}) \tag{Eq. (1)} \\
 & = 1.8 \\
 & \text{GWP impact from methanol combustion, kg CO}_2 \text{ / kg methanol} \\
 & = 0.48 \frac{\text{kgCO}_2}{\text{kgBio-oil}} \times \frac{16.7 \text{ kgBio-oil}}{5.5 \text{ kgMethanol}} (\text{Figure4}) \\
 & = 1.47
 \end{aligned}$$

The pyrolysis plant operates at 49% efficiency based on 19 MJ/kg of biomass and 23.3 MJ/kg of bio-oil LHV and 1.15 MW of electricity generation for 7000 operating hours per year (Eq. (2) and Fig. 3). The overall efficiency of the distributed pyrolysis and centralised methanol synthesis plants is thus 30%: 61.5% × 49%. The total GWP is 120 g of CO₂ equivalent / MJ of energy output (Eq. (3)). The basis is the GWP values predicted in Eq. (1) and 20 MJ/kg and 23.3 MJ/kg of LHV of methanol and bio-oil, respectively. The net electricity generation of 1.15 MW from the distributed pyrolysis plant (Fig. 3) is scaled up to the bio-oil processing capacity of the centralised plant, 16.7 kt/d of bio-oil, in the overall

conversion of input to output energy in Eq. 3. The GWP of FT liquid synthesis from biomass is 127 g of CO₂ equivalent / MJ of energy output.

Efficiency of pyrolysis plant %

$$= \frac{1.15 \times 3600 \times \frac{7000}{365} + 23.3 \times 132 \times 1000}{19 \times 340 \times 1000} \times 100 \quad \text{Eq. (2)}$$

$$= 49$$

GWP g CO₂ / MJ

$$= (2.18 + 1.8 + 1.47) \text{ (from equation 1)} \times \frac{5.5 \times 20 \text{ (Figure 4)}}{1.15 \times 3600 \times \frac{7000}{365} \times \frac{16700}{132 \times 10^6} + 23.3 \times 16.7 \times 0.615} \times 1000 \quad \text{Eq. (3)}$$

$$= 120$$

An equivalent natural gas based centralised system requires 0.64 kg of natural gas for the production of 1.5 MJ of CHP and 1 kg of methanol (yield = 0.782 mol of methanol / mol of natural gas with LHV = 50.17 MJ/kg)³⁶. The carbon dioxide and water vapour emissions are 82 g/MJ and 67 g/MJ of energy output, respectively, contributing to GWP of 87 g of CO₂ equivalent / MJ of energy output. Thus, a minimum of 0.49 kg CO₂ sequestration (capture) by 1 kg of woody biomass (LHV = 19 MJ/kg) is necessary to achieve 60% emission saving from the given biomass-bio-oil based methanol synthesis systems in Figs. 2-4, compared to a natural gas based system (Eq. (4)). This is without the consideration of the emission from LNG terminals and the transportation and material of construction of both systems.

Net CO₂ sequestration, kg / kg biomass

$$= \frac{(120 \text{ (from equation 3)} - 87 \times 0.4)}{1000} \frac{\text{kg}}{\text{MJ}} \times 19 \times 0.3 \text{ (overall system energy efficiency)} \quad \text{Eq. (4)}$$

$$= 0.49$$

If the efficiency of a biomass conversion system is increased from 30% to 60% (direct biomass utilisation in gasification has been demonstrated to exhibit higher energy efficiency of 54-58% for 367 MW systems³⁷), the net CO₂ sequestration (capture) requirement during biomass growth decreases from 0.49 to 0.29 kg CO₂ sequestration / kg of biomass, in order to achieve a minimum of 60% emission saving (Fig. 5). The feasible region in Fig. 5 is above the line that sets the minimum CO₂ sequestration requirement to achieve GHG emission savings by 60%, in order to comply with the EU Renewable Energy Directive for eligibility to be considered for the 2020 target of 10% renewable energy in

transport². Such an analysis may thus be extended for the selection of biomass, regions to grow and conversion systems, once land use-ecological information on forestry systems (e.g. rate of CO₂ sequestration or capture during the growth of a biomass) and systems analysis results can be coherently deduced. The effect of land usage for growing biomass on carbon (C) balances is under scrutiny and this includes the management of short rotation woody biomass crops. Limited information from short-rotation plantations available leads to a hypothesis that after ~10 years of such plantations soil C is increased by almost 10-25 Mg/ha³⁸ (1 Mg = 1 Megagram = 10⁶ g = 1 t). Based on 13.5 t/ha growth of short rotation coppice, the rate of CO₂ reduction from the atmosphere is 2.7-6.8 t CO₂ / t biomass. This is way above the CO₂ sequestration requirement by woody biomass for achieving the EU Directive's minimum GHG emission reduction target of 60% to be eligible for the 2020 target of 10% renewable energy in transport. This indicates complete removal of GHG emission by the use of these biofuel systems, compared to an equivalent lowest carbon fossil fuel, natural gas based system. Taking account of 0.75 kg of CO₂ removal per kg of bio-oil in the centralised methanol synthesis plant (Fig. 4), such biofuel systems can become a net carbon sink. Therefore, the economic sustainability of these systems should also be enhanced by versatile price banding of renewable energy technologies and products, as opposed to the single price structure for electricity offered by the UK Renewable Obligation Certificate³⁹. The mechanism has started to recognise the importance of receiving different levels of support for different technologies, providing a greater incentive to those that are further from the market with potential to deploy on a large scale. Typically, 50-70 Euro/t more COP of methanol from biomass-bio-oil is obtained²⁰, compared to 250 Euro/t of contract price of methanol in the European region, according to Methanex, valid from 1st April to 30th June, 2010⁴⁰.

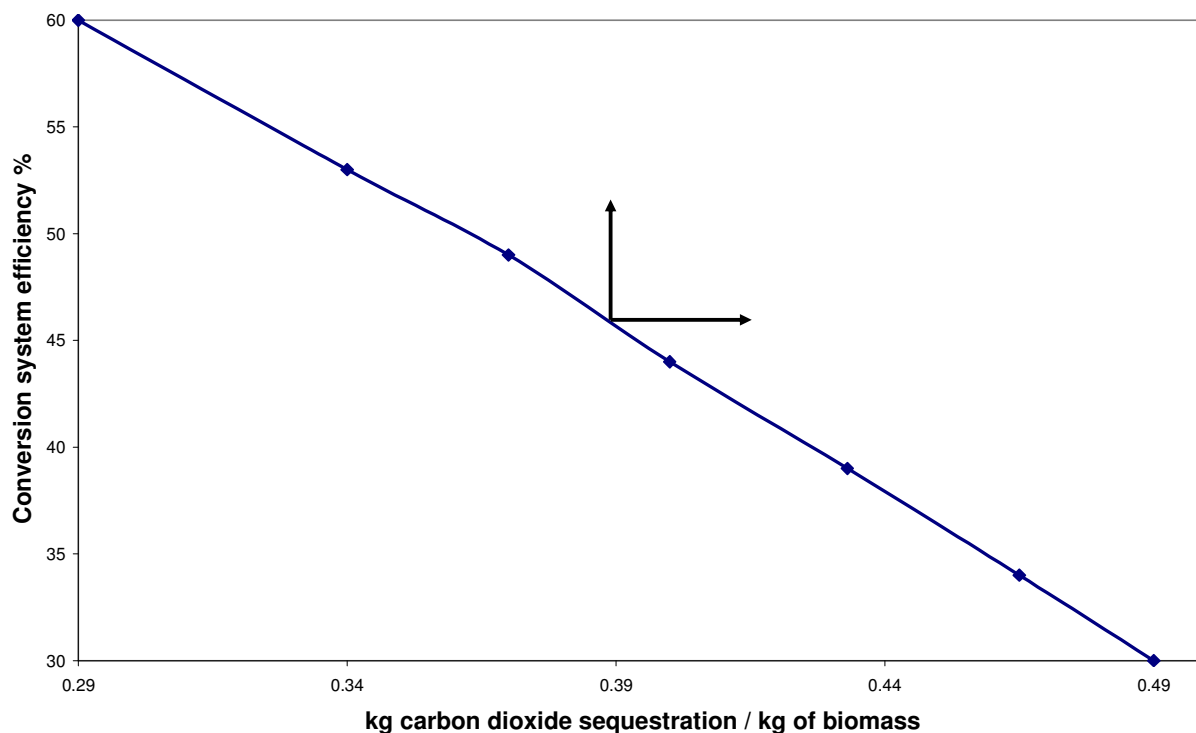


Figure 5. Conversion system efficiency vs. net CO₂ sequestration / capture requirement during biomass growth for achieving a minimum of 60% GHG emission saving

3. PROCESS SIMULATION BASED ANALYSIS OF BIO-OIL UPGRADER SYSTEMS

Compared to the bio-oil gasification route, bio-oil upgrader has relatively higher technical barrier to overcome. This lies in the efficiency of hydrogen supply for stabilising bio-oil, by reducing its oxygen content from 35-40 wt% to 2 wt%²³. The hydrogen requirement is 5% of the weight of bio-oil. This calls for almost an equal amount of bio-oil to fulfil the need for hydrogen, lowering the efficiency to 50%. Some of the lost efficiencies in a bio-oil upgrader can be recovered by infrastructural integration and share of facilities in a gasification route, for the generation of CHP and hydrogen (Fig. 2). Alternatively, if stable pyrolysis oil and the off-gas (fuel gas) from bio-oil upgrader are transferred to an existing refinery and in return refinery provides lower-cost hydrogen for the upgrader, the capital investment for the upgrader is reduced by 38% and the production cost of biofuel by 15%²³.

The hydrogen requirement by the commercially available refinery hydrocracker technologies, offered by Chevron, UOP, Shell, Exxon, etc., (Table 1) varies between 0.7-4% of the weight of hydrocracker feed, with higher amounts required for higher naphtha yield from heavier feedstock²⁶. The upgrader

technologies need to be established for future deployment, given their environmental incentives in terms of fossil resource preservation and emission reduction, illustrated as follows.

3.1 Bio-Oil Upgrader Process Simulation

Results of a stand-alone upgrader process simulation framework developed in Aspen Plus®⁴¹ (Fig. 6) based on parameters provided in Table 2 are presented in Table 3. The composition of bio-oil comprising of pyro-lignin, cellobiose, levoglucosan, furfural, hydroxyacetone, acetic acid and water, inputted in Aspen simulation, was approximated using linear regression based on bio-oil analysis in PNNL study²³, in Table 3. The bio-oil is upgraded to diesel and gasoline using hydrotreating (HYDROTREA) at 250°C and 172 bar and hydrocracking (HYDROGRA) at 675°C and 87 bar. Both the reactors were modelled as a stoichiometric reactor in Aspen Plus, in Fig. 6. Their hydrogen requirements are 19.43 kmol/t of bio-oil (64% excess supply is required to maintain the pressure) and 1.34 kmol/t of bio-oil (4 times excess supply required), respectively. Hence, 12.43 kmol/t and 5.36 kmol/t of bio-oil of unreacted hydrogen can be recovered from the two processes respectively, by pressure swing adsorption (B1), whilst the balance is produced by steam reforming (in FURNACE) of the off-gases (8, GAS1, GAS2, GAS3 and GAS4) recovered from the flash drums, B5, FLASH1, FLASH2, FLASH3 and B13, that are followed by the separation columns, debutaniser: DEBUTANE, naphtha splitter: NAPHSPLT and diesel splitter: DIESELSP. WATER (472 kg/t bio-oil) is recovered from WATERSEP (a decanter) into STEAM (224 kg/t of bio-oil) for the steam reformer and the rest into low pressure (LP) steam, utilising 452 kWh/t bio-oil of exothermic heat of reaction from HYDROTREA and 123 kWh/t bio-oil of heat of reaction from the decanter, respectively. However, an additional high grade heat of 364 kWh/t bio-oil at 700°C is required by the FURNACE, which may be supplied from the combustion of natural gas or combustion of additional biomass, lowering the renewability or overall efficiency of the system, respectively.

Table 3. Results of analysis of main streams in bio-oil upgrader Aspen simulation (stream 5 validated against streams 212, 213, 215, 220 and 221 in PNNL study²³)

COMPONENT NAMES	FORMULA	ASPEN NAMES	t/d	BIOOIL	GASOLINE	DIESEL	5	PNNL	2	2DEBUTAN	308	10
WATER	H2O	WATER	350.1	1.8	0.0	783.0	783.1	3.3	1.8	0.0	1.5	
HYDROGEN	H2	HYDRO-01	0.0	0.0	0.0	41.5	41.8	41.4	0.0	0.0	60.1	
CARBON-DIOXIDE	CO2	CARBO-01	0.0	0.2	0.0	98.0	98.0	95.2	0.4	0.0	95.0	
CARBON-MONOXIDE	CO	CARBO-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
OXYGEN	O2	OXYGE-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
NITROGEN	N2	NITRO-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
METHANE	CH4	METHA-01	0.0	0.0	0.0	36.5	36.5	36.5	0.0	0.0	36.5	
ETHANE	C2H6	ETHAN-01	0.0	0.1	0.0	22.2	21.8	22.2	0.1	0.0	22.1	
PROPANE	C3H8	PROPA-01	0.0	0.4	0.0	18.6	18.6	18.4	0.4	0.0	18.0	
N-BUTANE	C4H10-1	N-BUT-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
N-HEPTANE	C7H16-1	N-HEP-01	0.0	16.7	3.1	35.7	35.7	35.7	19.8	0.0	16.0	
ISOBUTANE	C4H10-2	ISOBU-01	0.0	0.8	0.0	16.4	16.4	16.3	0.9	0.0	15.5	
2,5-XYLENOL	C8H10O-7	2:5-X-01	0.0	0.7	82.9	87.1	87.1	84.4	83.6	0.0	0.8	
1-TRANS-3,5-TRIMETHYLCYCLOHEXANE	C9H18	1-TRA-01	0.0	5.9	37.5	53.3	53.3	53.3	43.4	0.0	9.9	
3,3,5-TRIMETHYLHEPTANE	C10H22-2	3:3:5-01	0.0	1.4	18.0	21.7	21.7	21.7	19.5	0.0	2.3	
N-PROPYLCYCLOHEXANE	C9H18-1	N-PRO-01	0.0	3.4	44.5	53.3	53.3	53.3	47.9	0.0	5.4	
1,3,5-TRIMETHYLBENZENE	C9H12-8	1:3:5-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
1,2,3-TRIMETHYLBENZENE	C9H12-6	1:2:3-01	0.0	0.2	6.4	7.0	7.0	7.0	6.6	0.0	0.4	
N-BUTYLCYCLOHEXANE	C10H20-1	N-BUT-02	0.0	0.1	2.4	2.6	2.5	2.6	2.4	0.0	0.1	
1,2-DIMETHYL-3-ETHYLBENZENE	C10H14-D3	1:2-D-01	0.0	0.3	17.3	18.0	17.3	18.0	17.6	0.0	0.5	
CIS-DECALIN	C10H18-1	CIS-D-01	0.0	0.5	33.2	34.7	34.7	34.7	33.7	0.0	1.0	
1-TRIDECENE	C13H26-2	1-TRI-01	0.0	0.4	93.2	94.1	94.0	94.1	93.6	0.0	0.4	
1,2,4-TRIETHYLBENZENE	C12H18-D6	1:2:4-01	0.0	0.2	34.1	34.7	34.7	34.7	34.4	0.0	0.3	
BICYCLOHEXYL	C12H22	BICYC-01	0.0	0.0	3.6	3.6	2.6	3.6	3.6	0.0	0.0	
DIPHENYL	C12H10	DIPHE-01	0.0	0.1	47.5	47.7	47.7	47.7	47.6	0.0	0.1	
DIAMANTANE	C14H20	DIAMA-01	0.0	0.3	92.7	94.1	94.0	94.1	93.0	0.0	1.0	
PHENANTHRENE	C14H10-2	PHENA-01	0.0	0.0	66.2	66.3	66.3	66.3	66.3	0.1	0.0	
CHRYSENE	C18H12	CHRY-01	0.0	0.0	25.6	67.5	66.6	67.5	67.5	42.0	0.0	
1-PENTENE	C5H10-2	1-PEN-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
O-XYLENE	C8H10-1	O-XYL-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
CYCLOPENTANE	C5H10-1	CYCLO-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
N-PENTADECANE	C15H32	N-PEN-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
N-OCTADECANE	C18H38	N-OCT-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
1,2,3,4-TETRAHYDRONAPHTHALENE	C10H12	1:2:3-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
ETHYLBENZENE	C8H10-4	ETHYL-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
TOLUENE	C7H8	TOLUE-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
BENZENE	C6H6	BENZE-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
P-XYLENE	C8H10-3	P-XYL-01	0.0	3.7	11.8	18.9	18.9	18.9	15.5	0.0	3.5	
N-PROPYLBENZENE	C9H12-1	N-PRO-02	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
N-BUTYLBENZENE	C10H14-1	N-BUT-03	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
1-METHYL-2-ETHYLBENZENE	C9H12-3	1-MET-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
1-TRANS-3,5-TRIMETHYLCYCLOHEXANE	C9H18	1-TRA-02	0.0	0.0	28.2	0.0	0.0	0.0	0.0	0.0	18.2	
METHYLCYCLOHEXANE	C7H14-6	METHY-01	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	
DEXTROSE	C6H12O6	DEXTR-01	444.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
FORMIC ACID	CH2O2	FORMI-01	25.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
PHENOL	C6H6O	PHENO-01	545.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
FURFURAL	C5H4O2	FURFU-01	126.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
ACETIC ACID	C2H4O2	ACETH-01	92.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
HYDROXYACETONE	C3H6O2	ACETO-01	65.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total Flow t/d			1650.4	37.4	648.1	1756.7	1753.6	971.2	699.7	42.1	308.8	
Average MW			51.6	85.1	151.2	23.4	23.4	30.8	149.0	228.1	8.5	
Centane number			12.9	26.0	28.9	24.4	24.4	12.8	28.7	15.5	12.8	
API			2.2	60.6	30.6	57.7	57.7	95.2	30.1	6.5	255.1	
Reid Vapour Pressure bar			0.1	1.1	0.1	2265.4	2279.8	5504.9	2.4	0.0	6925.5	

Table 4. Hypothetical overall reaction steps for bio-oil hydrotreater (HYDROTREA) and hydrocracker (HYDROCRA in shaded rows)

Reaction extent % molar	Reference component	Stoichiometry
37.6	DEXTROSE	3 HYDRO-01 + DEXTR-01 --> 5.25 WATER + 0.75 2:5-X-01
19.6	DEXTROSE	DEXTR-01 + .666666667 HYDRO-01 --> 3.333333333 WATER + 1.333333333 CARBO-01 + .333333333 DIAMA-01
12.4	DEXTROSE	0.333333333 HYDRO-01 + DEXTR-01 --> 4 WATER + CARBO-01 + 0.333333333 METHA-01
9.4	DEXTROSE	6 HYDRO-01 + DEXTR-01 --> 6 WATER + 0.666666667 1-TRA-01
9.4	DEXTROSE	6 HYDRO-01 + DEXTR-01 --> 6 WATER + 0.666666667 N-PRO-01
4.1	DEXTROSE	DEXTR-01 + 2 HYDRO-01 --> 4 WATER + CARBO-01 + .5 METHA-01 + .5 1:2:3-01
3.6	DEXTROSE	4.5 HYDRO-01 + DEXTR-01 --> 5 WATER + 0.5 CARBO-01 + 0.5 METHA-01 + 0.5 CIS-
2.0	DEXTROSE	DEXTR-01 + 2.333333333 HYDRO-01 --> 3.333333333 WATER + 1.333333333 CARBO-01 + .333333333 METHA-01 + .333333333 1-TRI-01
1.2	DEXTROSE	DEXTR-01 + 5 HYDRO-01 --> 5 WATER + .5 CARBO-01 + .5 METHA-01 + .5 N-BUT-02
0.8	DEXTROSE	5.5 HYDRO-01 + DEXTR-01 --> 6 WATER + 0.5 BICYC-01
95.4	FORMIC ACID	FORMI-01 + 1.75 HYDRO-01 --> .25 ETHAN-01 + .25 METHA-01 + .25 CARBO-01 + 1.5 WATER
4.6	FORMIC ACID	HYDRO-01 + FORMI-01 --> WATER + 0.5 CARBO-01 + 0.5 METHA-01
15.7	PHENOL	4 HYDRO-01 + PHENO-01 --> WATER + 0.46153846 1-TRI-01
15.3	PHENOL	PHENO-01 --> WATER + 0.333333333 CHRYS-01
13.6	PHENOL	2.28571429 HYDRO-01 + PHENO-01 --> WATER + 0.42857143 DIAMA-01
10.7	PHENOL	0.5 HYDRO-01 + PHENO-01 --> WATER + 0.5 DIPHE-01
10.4	PHENOL	1.333333333 HYDRO-01 + PHENO-01 --> WATER + 0.333333333 ISOBU-01 + 0.333333333
7.4	PHENOL	2.5 HYDRO-01 + PHENO-01 --> WATER + 0.5 1:2:4-01
7.2	PHENOL	PHENO-01 + 2.833333333 HYDRO-01 --> WATER + .166666667 ETHAN-01 + .166666667 N-HEP-01 + .166666667 PHENA-01 + .166666667 1-TRI-01
6.9	PHENOL	4 HYDRO-01 + PHENO-01 --> WATER + 0.666666667 1-TRA-01
6.9	PHENOL	4 HYDRO-01 + PHENO-01 --> WATER + 0.666666667 N-PRO-01
4.1	PHENOL	1.75 HYDRO-01 + PHENO-01 --> WATER + 0.75 P-XYL-01
0.5	PHENOL	PHENO-01 + 3.333333333 HYDRO-01 --> .333333333 WATER + .333333333 CARBO-01 + .333333333 ISOBU-01 + .333333333 1-TRI-01
0.4	PHENOL	3.5 HYDRO-01 + PHENO-01 --> WATER + 0.5 BICYC-01
0.4	PHENOL	HYDRO-01 + PHENO-01 --> 0.25 WATER + 0.75 2:5-X-01
0.2	PHENOL	2 HYDRO-01 + PHENO-01 --> WATER + 0.666666667 1:2:3-01
0.2	PHENOL	PHENO-01 + 5.5 HYDRO-01 --> WATER + .5 METHA-01 + .5 ISOBU-01 + .5 N-HEP-01
31.3	FURFURAL	4.5 HYDRO-01 + FURFU-01 --> 2 WATER + 0.5 CIS-D-01
23.2	FURFURAL	5.5 HYDRO-01 + FURFU-01 --> 2 WATER + 0.5 3:3:5-01
20.4	FURFURAL	3.5 HYDRO-01 + FURFU-01 --> 2 WATER + 0.5 1:2-D-01
13.9	FURFURAL	10 HYDRO-01 + FURFU-01 --> 2 WATER + 5 METHA-01
10.8	FURFURAL	4 HYDRO-01 + FURFU-01 --> CARBO-01 + METHA-01 + PROP A-01
0.5	FURFURAL	5 HYDRO-01 + FURFU-01 --> 2 WATER + 0.5 N-BUT-02
61.6	ACETIC ACID	ACETH-01 + 1.5 HYDRO-01 --> WATER + .5 CARBO-01 + .5 METHA-01 + .5 ETHAN-01
38.4	ACETIC ACID	ACETH-01 + 2.222222222 HYDRO-01 --> 1.777777778 WATER + .111111111 CARBO-01 + .111111111 METHA-01 + .111111111 ETHAN-01 + .111111111 PROP A-01 + .111111111 ISOBU-01 + .111111111 N-HEP-01
96.6	HYDROXYACETONE	ACETO-01 + 2 HYDRO-01 --> .25 N-HEP-01 + .25 PROP A-01 + .25 METHA-01 + .25 CARBO-01 + 1.5 WATER
3.4	HYDROXYACETONE	5 HYDRO-01 + ACETO-01 --> 2 WATER + 3 METHA-01
1	PHENANTHRENE	9 HYDRO-01 + PHENA-01 --> 2 METHY-01
1	CHRYSENE	12 HYDRO-01 + CHRYS-01 --> 2 1-TRA-02
0.1	METHYLCYCLOHEXANE	2 METHY-01 --> 3 HYDRO-01 + N-BUT-01 + 1:2:3-02

The biofuel fractions include GASOLINE, 15, 13 and 20 from FLASH1, FLASH2, FLASH3 and B13, respectively, in Fig. 6. Their characterisation properties equivalent to petroleum fractions, such as, API gravity, Reid Vapour Pressure, Volumetric Average Boiling Point, Flash Point, Aniline Point and Cetane Number derived using Aspen Properties (Prop-Sets), APISTD, RVP-API, VABP, FLPT-API, ANIL-API and CETANENO, respectively, are presented in Table 5. In the case presented in Fig. 6 and Table 3, streams 15, 13 and 20 are blended into diesel pool and GASOLINE into gasoline pool. Validation in terms of stream 5 analysis and property specifications against stream nos. 212, 213, 215, 220 and 221 in PNNL study results²³ is presented in Table 3. The above characterisation properties of the streams were also predicted using Aspen simulation, in Table 3. Table 5 highlights probable blending cases and properties. 10% by weight of the DIESEL in Fig. 6 (stream name: 20 & 15 & 13) when blended with refinery diesel (REF DIESEL), gives rise to the stream ‘20 & 15 & 13 & REF DIESEL’, with acceptable diesel properties, specific gravity: 0.825, flash point: 76.7°C and cetane number: 56.9. Another blending case with ‘GASOLINE & 20’ blended in gasoline pool is viable considering that stream 20 displays closer to heavy naphtha properties, such as specific gravity of 0.777 and volumetric average boiling point

of 140.5°C. The remaining diesel pool, 15 & 13, when blended with 90% REF DIESEL, obeys diesel specifications (specific gravity of 0.826; cetane number of 56.8) adequately.

Table 5. Gasoline, diesel and hydrocracker feed blending scenarios

STREAM NAME	GASOLINE	20	15	13	GASOLINE & 20	BIO-OIL BASED BLENDING	
						15 & 13	20 & 15 & 13
FLOW RATE t/d	37.4	28.2	210.8	409.1	65.7	619.9	648.1
SPECIFIC GRAVITY	0.737	0.777	0.842	0.897	0.754	0.878	0.873
APISTD	60.6	50.6	36.5	26.2	56.3	29.7	30.6
RVP-API bar	1.1	0.7	0.1	0.0	0.9	0.1	0.1
VABP C	115.0	140.5	191.5	250.4	126.0	229.6	225.2
FLPT-API C	-38.0	18.2	42.8	71.8	-13.9	53.5	46.8
ANIL-API C	44.7	43.3	31.9	26.4	44.1	28.0	28.0
CETANENO	26.0	30.9	30.9	26.1	28.1	28.4	28.9

STREAM NAME	10% BLENDING OF BIO-OIL BASED DIESEL TO REF DIESEL			HYDROCRACKER FEED			
	REF DIESEL	15 & 13 & REF DIESEL	20 & 15 & 13 & REF DIESEL	15 & REF DIESEL	308	13 & 308 BLEND	REFINERY
FLOW RATE t/d	1896.8	6198.6	6481.1	2107.6	42.1	451.2	
SPECIFIC GRAVITY	0.82	0.826	0.825	0.822	1.025	0.909	0.970
APISTD	41.1	39.9	40.0	40.6	6.5	24.3	14.4
RVP-API bar					0.0	0.0	
VABP C					440.8	268.2	414.5
FLPT-API C	80	77.4	76.7	76.3	146.1	78.8	152.8
ANIL-API C					48.7	28.5	64.5
CETANENO	60	56.8	56.9	57.1	15.5	25.1	32.2

The PNNL study demonstrated that 38% saving in capital is achievable if the hydrocracker is a shared facility within a nearby refinery²³. In that case, stream 308 can be sent to a refinery as a hydrocracker feed, whilst GASOLINE and '15 & 13' can be recovered as gasoline and diesel, respectively, from the bio-oil upgrader (Fig. 6 and Tables 3 and 5). The stream 308 displays slightly heavier properties than a usual refinery hydrocracker feed, e.g. API gravity of 6.5 compared to 14.4 and cetane number of 15.5 compared to 32.2, respectively (Table 5), requiring the refinery hydrocracker more appropriate for cocker heavy cycle gas oils²⁶. Alternatively, stream 13 can be freed from the diesel pool and blended with stream 308 as a refinery hydrocracker feed in the upgrader. This improves both the properties of '15 & REF DIESEL' after 10% blending of bio-oil based diesel with 90% of REF DIESEL, e.g. specific gravity of 0.822 and cetane number of 57.1, as well as, '13 & 308 BLEND' to be considered as a refinery hydrocracker feed, e.g. API gravity of 24.3 and cetane number of 25.1. The blending decisions would depend on the economic incentives of the bio-oil upgrader from the selling of gasoline, diesel and hydrocracker feed to a nearby refinery as well as refiners restructuring, expansion and green future strategies.

4. ECONOMIC ANALYSIS OF BIO-OIL UPGRADER PROCESS

Fig. 7 depicts a bio-oil upgrader case, wherein the following streams in Fig. 6, ‘WATER’ after heat recovery from ‘HYDROTREA’, ‘8’ after hydrogen separation from pressure swing adsorption and ‘2DEBUTAN’ are the end products, present LP steam, Off-gas and Stable oil, respectively. The HYDROTREA operating at 250°C and 100 bar generates an exothermic heat of reaction of 452 kWh/t bio-oil, from which 293 kWh/t bio-oil or 0.472 tonne of LP steam at 210°C and 15 bar per tonne of bio-oil is generated (Eq. (5)). The balance of the heat from HYDROTREA (159 kWh/t bio-oil) and the heat available from the decanter (123 kWh/t bio-oil) is recovered into 282 kWh/t of LP steam generation per tonne of bio-oil. Hence, the total heat available from the upgrader site in Fig. 7 is 575 kWh/t.

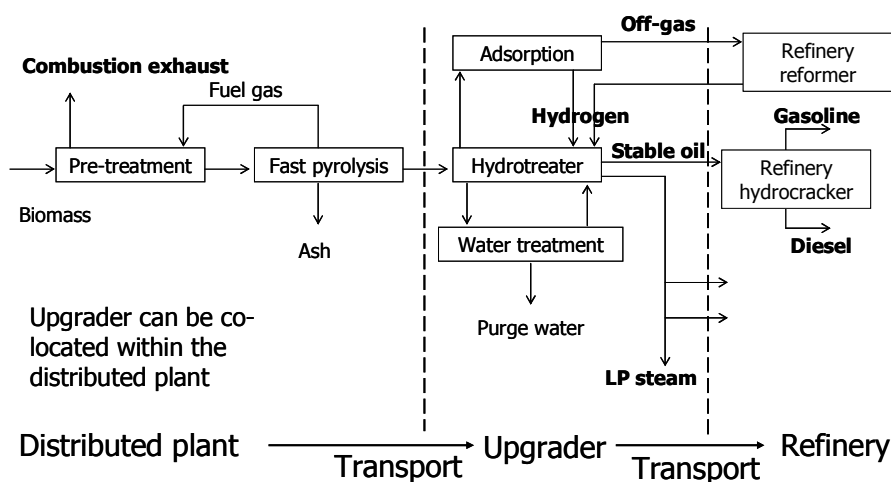


Figure 7. Integration synergy between bio-oil upgrader and refinery

On 90% recovery on molar basis of the unreacted hydrogen from the product stream 8 of the flash drum, B5, using pressure swing adsorption, 11.2 kmol of hydrogen per tonne of bio-oil is produced. The remaining off-gas, 5.06 kmol/t bio-oil, can be sold as a reformer feed to a nearby refinery. The balance of hydrogen required by HYDROTREA, 20.67 kmol/t bio-oil, can be supplied from the refinery reformer at a discounted price.

The stable oil (2DEBUTAN) contains 2.3 wt% oxygen, compared to ~37 wt% in the bio-oil, based on the compositions provided in Table 3. Its petroleum equivalent characterisation properties, e.g. 30.1 API and 28.7 CETANENO (Table 3), are also within an acceptable range to process through an existing refinery

hydrocracker (Table 5). The yields from the integrated bio-oil upgrader under consideration are calculated based on the material balance around WATERSEP and B5 in the bio-oil upgrader flowsheet in Fig. 6 and the various flowrates provided in Table 3 (Eq. (5)).

$$\begin{aligned}
 \text{Yield of Stable oil, \% bio-oil} &= \frac{699.7}{1650.4} \times 100 = 42.4 \\
 \text{Yield of LP steam, \% bio-oil} &= \frac{(783 - 3.3)}{1650.4} \times \frac{293 + 282}{293} \times 100 = 92.6 \\
 \text{Yield of Off-gas, \% of bio-oil} &= \frac{(971.2 - 699.7 - 0.9 \times 41.4)}{1650.4} \times 100 = 14.2
 \end{aligned}
 \tag{Eq. (5)}$$

The saving in the capital cost of the bio-oil upgrader due to integration with refinery is \$115 million for a bio-oil processing capacity of 1320 t/d or 2000 odt/d of biomass²³. The economic analysis for the bio-oil upgrader system is presented in US \$ for comparison against the PNNL study²³. A conversion factor of 1 Euro = 1.23 \$ is used to convert the economic data provided in the following sections. This study extends the economic analysis to a business model between refiner and upgrader to create a win-win scenario.

The COP of upgrader products depends on the cost of biomass (75 \$/t) and the annual capital cost of an integrated upgrader (Eq. 6). The annual capital cost is evaluated by multiplying the capital cost of an equivalent integrated upgrader, \$188 million in Table 7.1 of PNNL study²³ with Annualised Capital Charge (ACC). Further, Discounted Cash Flow (DCF) calculations¹³⁻¹⁴ based on three operating years, 10, 15 and 25, and variation in Internal Rate of Return (IRR) between 10-20%, are performed here, in order to obtain an ACC between 11.017% (minimum corresponding to 25 operating years and 10% IRR) and 23.852% (maximum corresponding to 10 operating years and 20% IRR). A flat rate of COP of the products from bio-oil upgrader, based on the works on the value analysis of process systems¹¹⁻¹⁴ is calculated using Eq. (6) (7000 operating hours/y or 19.178 hours/d). The variation in the COP for various investment strategies is projected in Fig. 8. The DCF for 10 operating years and 20% IRR is presented in the figure.

$$\text{Cost of production, \$ / t} = 75 + \frac{\% \text{ACC}}{100} \times \frac{188 \times 10^6}{1650.4} \times \frac{19.178}{7000}
 \tag{Eq. (6)}$$

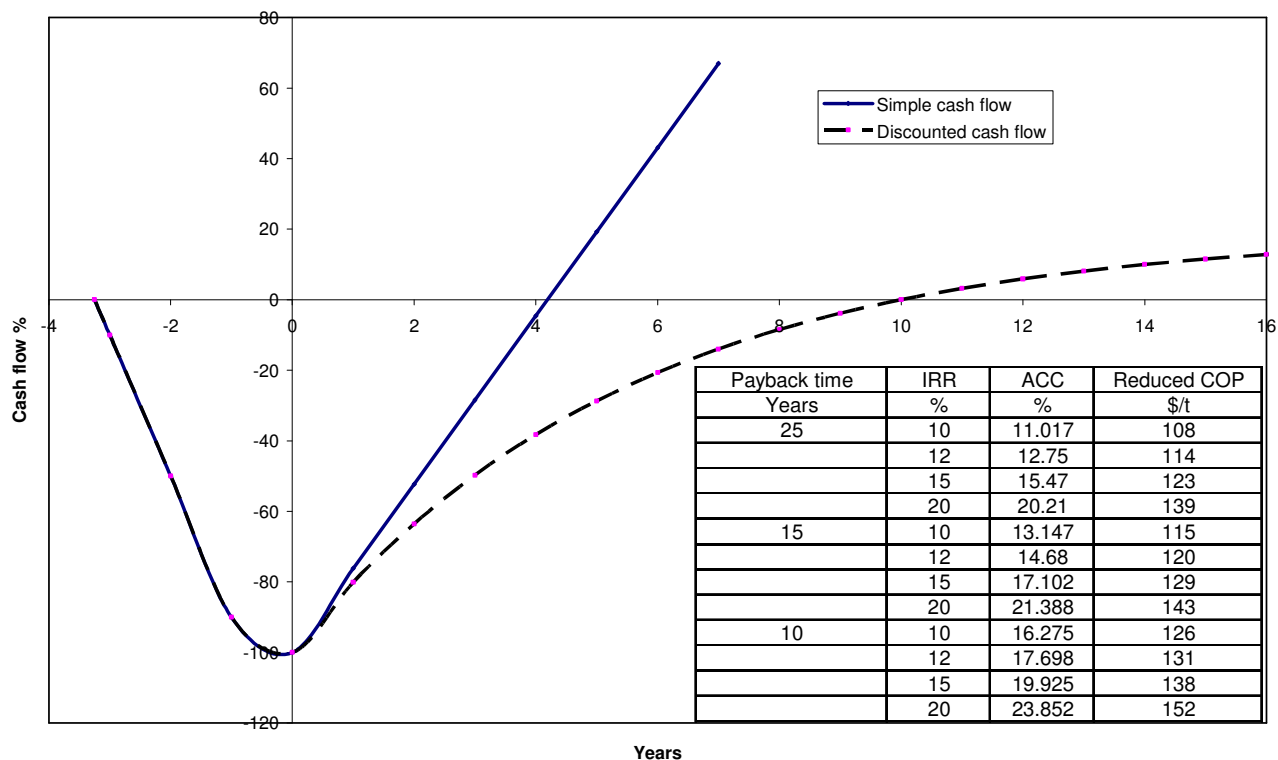


Figure 8. DCF calculations and variation of COP of products from bio-oil upgrader integrated with refinery

Thus, the COP predicted varies between 108 \$/t and 152 \$/t with the minimum and the maximum COP corresponding to the minimum and maximum %ACC in the DCF calculations, respectively (Fig. 8). Next, the distribution of COP to the various products, stable oil, LP steam and off-gas from the bio-oil upgrader is estimated by individual energy values and GWP impacts, in Figs. 9 and 10, respectively, in the following sections.

4.1 COP of Bio-Oil Upgrader Products by Energy Values

The energy values of the LP steam, off-gas and stable oil, 49.5 MW (or 575 kWh/t of bio-oil), 72.3 MW (840 kWh/t of bio-oil) and 328 MW (3811 kWh/t of bio-oil) respectively, are established from Aspen simulation. Their heating values are 1.5 MWh/t of LP steam, 7.5 MWh/t of off-gas and 11.2 MWh/t of stable oil, respectively. Thus, the ratios of the heating values between the off-gas and the LP steam and between the stable oil and the LP steam are 5 and 7.44, respectively. If the COP distribution is by energy values, the expression between an overall COP and the COP of individual products, LP steam (x), off-gas

($5x$) and stable oil ($7.44x$) can be deduced (Fig. 9). The energy efficiency thus obtained from an integrated bio-oil upgrader is 46%, based on 23.3 MJ/kg of LHV of bio-oil and 7000 operating hours per year.

4.2 COP of Bio-Oil Upgrader Products by GWP Impacts

The GWP from the off-gas is the lowest, 21.2 t/h of CO₂ equivalent, followed by, 48.4 t/h and 94.4 t/h from LP steam and stable oil, (0.246, 0.562 and 1.097 t/t of bio-oil) respectively. The COP distribution by GWP impacts to individual products is correlated to the overall COP, by the use of two GWP ratios between LP steam and off-gas and between stable oil and off-gas, 2.28 and 4.44, respectively, in Fig. 10. Fig. 11 compiles the maximum and minimum COP of individual products by energy values and GWP impacts. The ranges of COP of LP steam thus obtained are 17-24 \$/t and 73-103 \$/t, for off-gas: 85-120 \$/t and 32-45 \$/t and for stable oil: 127-178 \$/t and 143-201 \$/t, according to the energy values and GWP impacts, respectively. Obviously, the minimum and the maximum COP for each range correspond to 25 operating years and 10% IRR and 10 operating years and 20% IRR, respectively (Fig. 8). The selling prices of the bio-oil upgrader products, LP steam, off-gas and stable oil must be set above their maximum COP for a given DCF strategy, for economic feasibility. Thus, the minimum selling prices for the given case and ranges are 103 \$/t (according to GWP impact), 120 \$/t (according to energy value) and 201 \$/t (according to GWP impact), for LP steam, off-gas and stable oil, respectively.

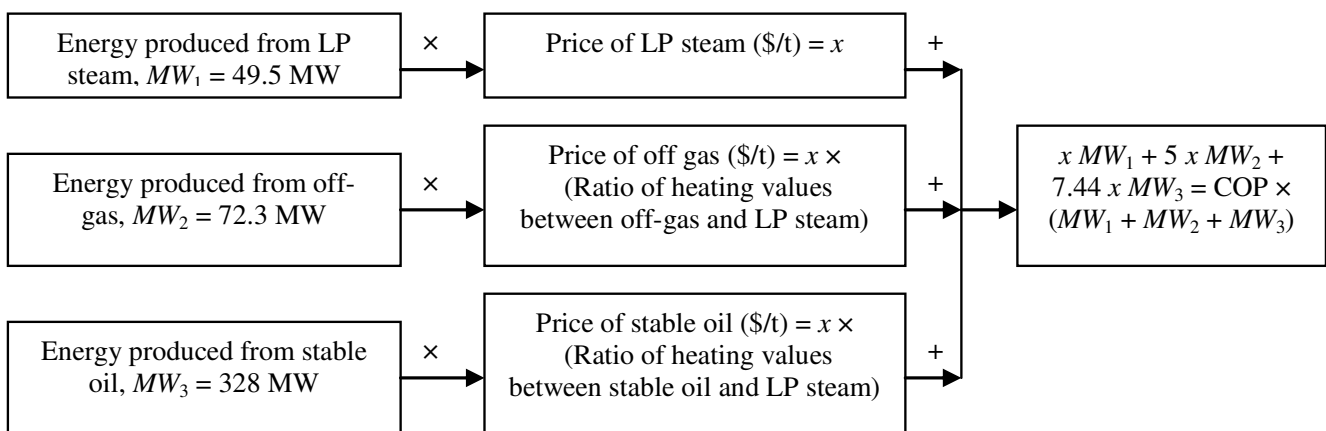


Figure 9. Distribution of COP to bio-oil upgrader products according to energy values

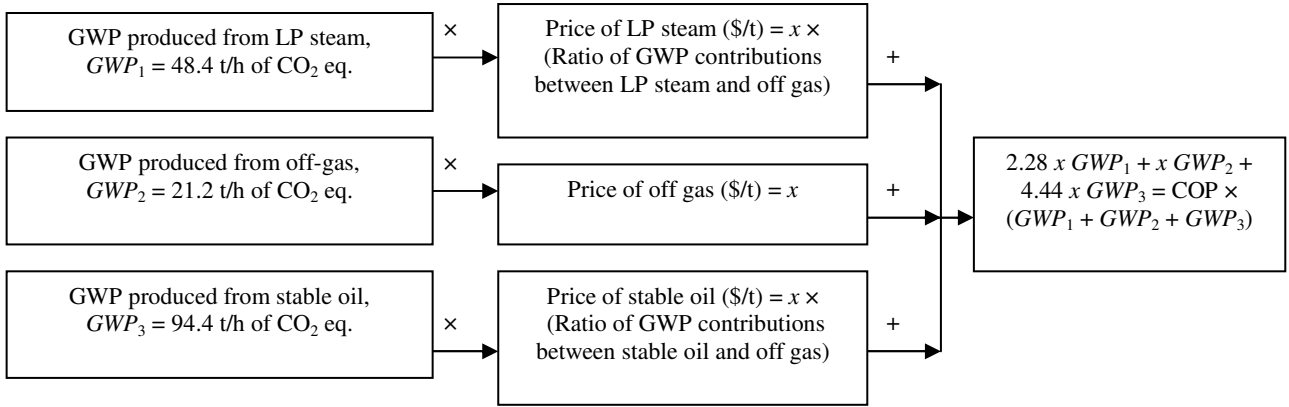


Figure 10. Distribution of COP to bio-oil upgrader products according to GWP impacts

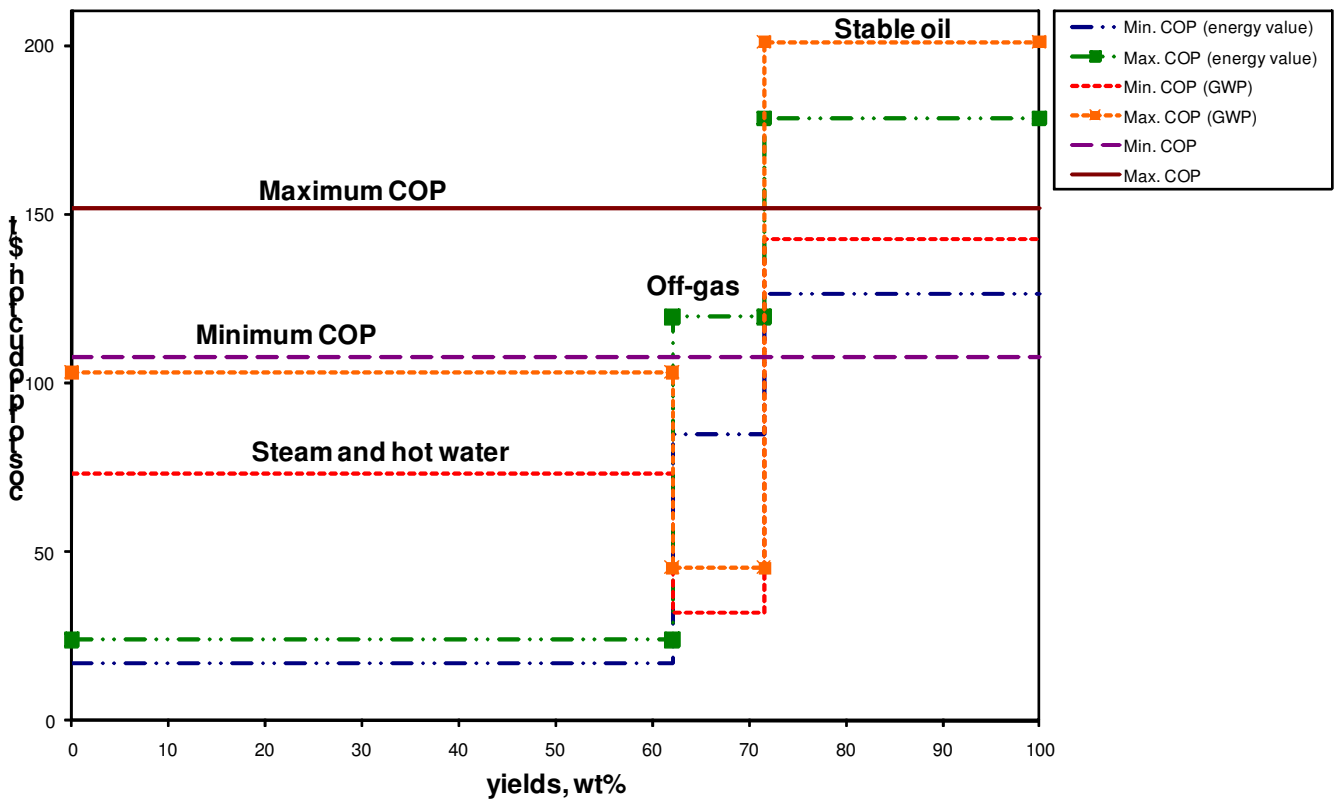


Figure 11. Maximum and minimum COP of individual products by energy values and GWP impacts

4.3 Analysis of Economic Feasibility of Co-Processing Between Bio-Oil Upgrader and Crude Oil Refinery

The COP of a refinery straight-run hydrocracker feed, 490 \$/t, is contributed majorly by the cost of crude oil, 98.04% or 480.19 \$/t based on 67 \$/bbl and 30 API gravity (specific gravity of 0.877) and only

slightly by the annualised capital cost of the crude oil distillation unit (CDU), 1.21% or 5.91 \$/t and its operating cost 0.75% or 3.68 \$/t (Table 6)¹¹⁻¹². The Brent spot price varied between 67 \$/bbl and 87 \$/bbl in Jan-May, 2010⁴². The tolling fees (or the annualised capital cost) of the CDU is predicted based on the following assumptions, ACC of 23.852% (Fig. 8), crude oil processing capacity of 15 kt/d, a single train CDU capacity of 100-180 kbbl/d, the cost of CDU unit of 1300 \$/bbl and 7000 operating hours/y or 19.178 operating hours/d. Eq. (7) provides the cost correlation to estimate the tolling fees for the CDU.

$$\begin{aligned}
 & \text{Capital cost of CDU, } \$/t \\
 & = 1300 \times \frac{23.852}{100} \times 100 \left(\frac{15}{0.877 \times 0.159 \times 100} \right)^{0.6} \frac{19.178}{15 \times 7000} \quad \text{Eq. (7)} \\
 & = 5.91
 \end{aligned}$$

The operating costs included the costs of electricity, low pressure steam, cooling water and fuel consumed by CDU (Table 6). The COP of refinery hydrocracker feed based on the straight run fractions is thus 490 \$/t.

Table 6. Operating, capital and crude oil costs for the prediction of COP of refinery hydrocracker feed

Cost contributors			\$/unit	\$/t
Power	kWh/t of crude oil	7.09	0.05	0.32
Low pressure steam	t/t of crude oil	0.10	2.10	0.20
Cooling water	m ³ /t of crude oil	1.45	0.03	0.04
Fuel	MJ/t of crude oil	0.45	6.89	3.11
Capital	\$/t of crude oil	5.91		5.91
Price of crude oil	\$/t	480.19		480.19
COP of refinery hydrocracker feed, \$/t				489.79

With the COP predicted for the upgrader products and the refinery hydrocracker feed using Eqs. (5)-(7) and based on the information in Figs. 6-11 and Tables 2-6, an acceptable selling price of the stable oil can be any value between 201 \$/t and 490 \$/t. For the refiner, 490 \$/t is the maximum acceptable buy-in price of a hydrocracker feed. If the bio-oil upgrader products, LP steam, off gas and stable oil are priced according to their heating values, y , $5y$ and $7.44y$ \$/t, respectively, the value of y must be such that the upgrader can exchange these three products for hydrogen (20.67 kmol of hydrogen / t of bio-oil) from the refinery. Alternatively, the bio-oil upgrader has to purchase hydrogen at a much higher market price, e.g. 1200 \$/t. Eq. 8 illustrates the expression between y and the given market price of hydrogen, and thereby

the estimated selling prices of LP steam, off gas and stable oil of 34.85 \$/t, 174.27 \$/t and 259.32 \$/t, respectively. Furthermore, an upgrader economic margin of 52.2 \$/t bio-oil or 7.3 \$/bbl equivalent crude oil is estimated. This margin is certainly competitive against oil refining margins, further illustrated as follows. Thus, co-processing and the proposed business model helped in raising the biorefining margin to level match with the petroleum refining margins. An alternative scenario is if the stable oil from the upgrader is sold to a refinery as a hydrocracker feed at its maximum acceptable buy-in price from refiner's perspective, 490 \$/t. This implies an additional upgrader margin of 97.8 \$/t bio-oil $\{= 0.424 \times (490 - 259.32)\}$ or 13.6 \$/bbl bio-oil equivalent crude oil. Thus, if the stable oil can be sold by the upgrader at 490 \$/t and hydrogen (20.67 kmol of hydrogen / t of bio-oil) is purchased at 1200 \$/t, an increased upgrader margin of 97.8 \$/t bio-oil or 13.6 \$/bbl bio-oil equivalent crude oil (compared to the refinery hydrogen exchange scenario) can be achieved. Thus, if stable oil from a bio-oil upgrader can be launched as a product / refinery hydrocracker feed, the upgrader can operate fully independently (e.g. purchase hydrogen from vendors at competitive rate). In this case however, refinery will have lower economic incentive than the former scenario (hydrogen exchange), discussed later. Thus, the main concern for the upgrader is the market acceptability of stable oil as a product.

Margin of bio-oil upgrader from stable oil, \$/t bio-oil

$$= 0.424(\text{from equation 5}) \times (7.44y - 178(\text{from Figure 11}))$$

Margin of bio-oil upgrader from LP steam, \$/t bio-oil

$$= 0.926 \times (y - 24)$$

Margin of bio-oil upgrader from off-gas, \$/t bio-oil

$$= 0.142 \times (5y - 120)$$

Eq. (8)

$$0.424 \times (7.44y - 178) + 0.926 \times (y - 24) + 0.142 \times (5y - 120) = \frac{20.67 \times 2.016}{1000} \times 1200$$

$$y = 34.85$$

Margin of bio-oil upgrader \$/t bio-oil

$$= 34.5 + 10.1 + 7.7 = 52.2$$

Upgrader margin (equivalent to crude oil) \$/bbl = 52.2 \times 0.877 \times 0.159 = 7.3

We now take Eq. 8 as a basis for the creation of win-win economic scenario for the refinery. The LP steam (0.926 t/t bio-oil from Eq. (5)) and the off-gas (0.142 t/t bio-oil) supplied from the upgrader to the refiner can be reformed into additional 61.5 kmol of hydrogen / t bio-oil. If this additional amount of hydrogen is sold directly to the market at 1200 \$/t, it would create an additional economic incentive of

12.8 \$/bbl or 91.8 \$/t of crude oil ($= \frac{61.5 \times 2.016}{1000} \times 1200 - 34.85 \times 0.926 - 174.27 \times 0.142$) \$/t, without the

consideration of additional tolling fees (due to capital cost). This allows an additional spending capacity by 70% of the total purchasing cost of LP steam and off-gas for the refinery. This once again creates a win-win economic scenario against the bio-oil upgrader (52.2 \$ / t bio-oil in Eq. 8).

Considering strongly rising biodiesel demand, its prices are envisaged to rise from 75 \$/bbl to 88 \$/bbl (540-635 \$/t of biodiesel) within one year⁴³. Based on 259.32 \$/t of purchasing cost of stable oil (Eq. 8) or 270 \$/t of COP of renewable diesel produced from the co-processing of stable oil, the preliminary economic incentive of the co-processing over purchasing of biodiesel (at a minimum of 540 \$/t) for 10% biofuel blend is 22.7 \$/t or 3.2 \$/bbl of crude oil, based on 0.084 t renewable biofuel yield / t of crude oil for the given capacity and API gravity. As evident, combination of the two incentives, 12.8 \$/bbl from the additional hydrogen production and 3.2 \$/bbl from the replacement of final biodiesel blending by the renewable diesel production from the stable oil co-processing, makes the refinery economic incentive competitive against the bio-oil upgrader (7.3 \$/bbl in Eq. 8), even if refinery expansion is accounted for. 8.7 \$/bbl may be allowed for refinery expansion in order to create win-win economic scenario between the refinery and the upgrader. For the scenario with all hydrogen sold by the refinery (61.5 + 20.67) kmol / t of bio-oil at the market rate of 1200 \$/t and stable oil sold by the upgrader to the refinery at the market rate of 490 \$/t, 141.8 \$/t or 19.8 \$/bbl of crude oil of economic incentive from the selling of all the hydrogen and 39.3 \$/t or 3.3 \$/bbl of crude oil of economic incentive from the replacement of final biodiesel blending by the renewable diesel production from the stable oil co-processing are obtained. Comparing these values with the upgrader margin of 97.8 \$/t bio-oil or 13.6 \$/bbl bio-oil equivalent crude oil, 6.6 \$/bbl of crude oil (or 47.3 \$/t) will be available for refinery expansion. This is less in comparison to 8.7 \$/bbl of crude oil in hydrogen exchange scenario.

Given the volatile and vulnerable petroleum markets, oil companies are under pressure for moving towards greener future, within which refinery expansion strategy may be a commonplace. For 10% renewable diesel production from stable oil (0.084 t renewable biofuel / t of crude oil for the given capacity and API gravity) for blending into 0.757 t of refinery diesel pool per t of crude oil, 0.086 t of

imported stable oil and 1.35 kmol of hydrogen production per t of crude oil may be necessary, requiring 12% expansion of the refinery hydrocracker unit (Eq. (9) using GASOLINE, DIESEL and 2DEBUTAN yields in Table 3). Fulfilling the hydrogen requirements for the renewable diesel production within refinery and by the bio-oil upgrader may require refinery reformer capacity expansion by 10% and 50%, respectively. Therefore, flexibility in terms of external purchasing of hydrogen vs. paying the tolling fees to the refiner, by the bio-oil upgrader needs to be considered.

Stable oil import for 10% renewable diesel blending t/t crudeoil

$$= \frac{0.757}{0.9} \times 0.1 \times \frac{699.7}{(37.4 + 648.1)} = 0.086$$

Hydrocracker hydrogen requirement kmol/t crude oil

$$= 1.34 \times 5 \times 0.086 \times \frac{1650.4}{699.7} = 1.35$$

Eq. (9)

% expansion of refinery hydrocracker unit

$$= \frac{1}{9} \times \frac{1.07}{0.98} \times 100 = 12$$

5. ANALYSIS OF GHG EMISSION SAVINGS FROM CO-PROCESSING IN HYDROCRACKER

The hydrocracker co-processing unit and the combustion of fuels were analysed for an estimation of the environmental drivers, e.g. GHG impact reduction and crude oil saving and barriers, e.g. yield loss and land use, as a function of percentage blending of biofuel derived from stable oil. Table 7 provides a comparison of performance between refinery and stable oil hydrocrackers, in terms of yields and carbon dioxide emissions from the combustion of gasoline and diesel derived from respective processes and the combustion of natural gas used for the generation of electricity, heat and hydrogen. The analysis clearly shows environmental incentive in terms of saving in carbon dioxide from a total of 3316.46 kg/t of refinery hydrocracker feed to 189.45 kg/t of stable oil hydrocracked. The saving in carbon dioxide emission and crude oil, relative to without co-processing case, increases with increasing percentage of biofuel co-production: e.g. emission saving increases from 313 kg of CO₂ per tonne of hydrocracker feed in 10% biofuel co-production case to 1876 kg/t in 60% biofuel co-production case and crude oil saving from 141 to 845 kg/t, respectively. Henceforth, the bio-oil upgrader technology can only provide 31.3%

carbon dioxide saving for 10% biofuel blending and over 60% carbon dioxide saving for 20% biofuel blending, respectively. Additionally, the diesel and gasoline fuel yields are reduced due to low energy density of the upgrader products. The transportation fuel yield from a refinery hydrocracker is 98.9%, while that from a bio-oil upgrader is 70.6%. The projection of land use with respect to increasing bio-fuel blend is also shown for 13.5 t/ha growth of short rotation coppice, as before³⁸.

Table 7. Comparison of performance between refinery and stable oil hydrocrackers, in terms of yields and carbon dioxide emissions from the combustion of gasoline and diesel derived from respective processes and the combustion of natural gas used for generating electricity, heat and hydrogen

	Yields on hydrocracker feed		Natural gas for electricity	Natural gas for heat	Natural gas for H ₂ production
	Gasoline	Diesel			
	kg/t of feed	kg/t of feed	kg/t of feed	kg/t of feed	kg/t of feed
Refinery hydrocracker	113.20	876.30	1.41	56.79	0.09
CO ₂ emission from combustion	292.36	2863.78	3.88	156.18	0.26
Stable oil hydrocracker	38.50	667.30		68.89	
CO ₂ emission from combustion	-	-		189.45	

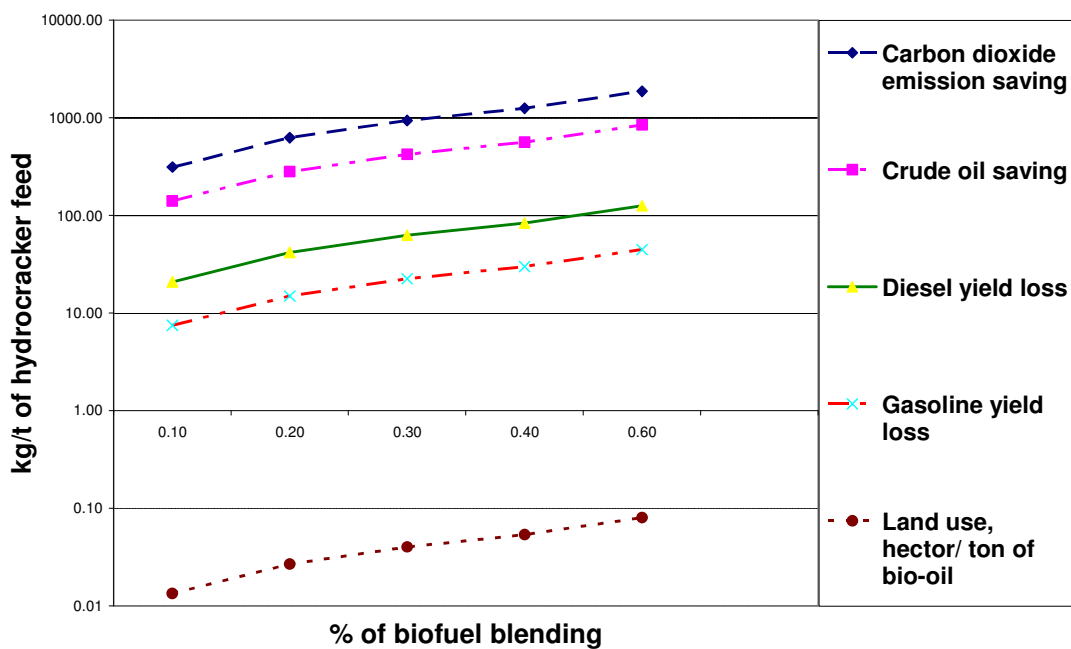


Figure 12. Increases in saving in carbon dioxide emission and crude oil, diesel and gasoline yield loss and land use with respect to percentage of biofuel blending in integrated bio-oil upgrader and refinery case

6. CONCLUSIONS

Conceptual process design and integration and sustainability analysis of industrial scale bio-oil gasification based systems and integrated bio-oil upgrading and refinery co-processing systems are presented. The biomass pyrolysis and bio-oil gasification based systems were analysed for adaptation to different commercial process technologies available. This analysis shows that multiple distributed biomass pyrolysis units and centralised bio-oil gasification based biofuel systems, methanol and FT liquid synthesis, can be synergistically integrated. The overall integrated scheme can eliminate the GHG emission completely, compared to an equivalent natural gas based system. Thus, the closer to market industrial scale bio-oil gasification based systems certainly can meet the EU Directive’s minimum GHG emission reduction target of 60% to be eligible for the 2020 target of 10% renewable energy in transport. The integrated bio-oil upgrading and refinery co-processing systems were evaluated using process simulation, integration and value analysis based approaches. Bio-oil upgrading is a two-step process

comprising of mild hydrotreating followed by hydrocracking. Hypothetical models for bio-oil composition and hydrotreating and hydrocracking reactions were proposed using linear regression. A stand-alone bio-oil upgrader that requires hydrogen by 5% of the weight of bio-oil and thereby an equal amount of bio-oil to fulfil the need for hydrogen, lowering the efficiency to 50%, is not an economically feasible option. Thus, this study was also aimed at developing integrated bio-oil upgrader and refinery co-processing options and business models to create win-win economic scenario between the two. Both the stand-alone and integrated upgrader conceptual flowsheets were designed to produce biofuels (gasoline and diesel) and stable oil (oxygen content reduced from 37 wt% in bio-oil to 2 wt% in stable oil), respectively, alongside LP steam and off-gas (fuel gas). The characterisation properties of the biofuels and stable oil produced meet the equivalent petroleum fraction properties in terms of API gravity, Reid Vapour Pressure, Volumetric Average Boiling Point, Flash Point, Aniline Point and Cetane Number, estimated using Aspen Properties (Prop-Sets). Once the mass and energy balance of the conceptual upgrader flowsheet was deduced, the COP of products was estimated based on their relative energy values and GWP impacts. Furthermore, the selling prices of upgrader products based on their relative energy values were determined for equalising economic incentives of the upgrader and the refinery. The economic incentive for the upgrader was generated by selling of its intermediate products, stable oil, LP steam and off-gas to the refinery and by the supply of refinery hydrogen without incurring any cost. Refinery's economic incentive was created from the selling of the excess hydrogen (after fulfilling upgrader hydrogen requirement) produced using reforming between off-gas and LP steam supplied from the upgrader and from saving from the co-processing over purchasing of biodiesel. A step-by-step and systematic economic analysis approach helped to arrive at an acceptable product selling price structure between upgrader and refinery. The GHG emission saving analysis of bio-oil upgrader and co-processing indicates that at least 20% blending of biofuel would be necessary to achieve 60% GHG emission saving compared to no biofuel blending case. Both the savings in GHG emission and crude oil reserve increase with the increasing biofuel proportion in transport, with the latter is saved by 14.1% and 84.5% in 10% and 60% biofuel blending cases, respectively.

ACKNOWLEDGEMENT

The authors would like to thankfully acknowledge contributions from PhD student Ms Yadira Lopez in the prediction of property sets using Aspen simulation and MSc student Ms Mariam Nuhu in the analysis of soil carbon capture for poplar plantation.

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