

Advanced Integrated Bio-Refineries (IBRs) and Sustainable Development (SD):

IBRs: Generation of Sustainable Alternatives.

A.Zayed¹, Mai M.K. Fouad¹ S.S.E.H. Elnashaie^{1,2,*}

¹Chemical Engineering Department, Cairo University, Giza, Egypt.

²Chemical / and Biological Engineering, University of British Columbia (UBC), Vancouver, Canada.

Received: 1 Jun. 2020, Revised: 19 Jul. 2020, Accepted: 15 Aug. 2020.

Published online: 1 Sep. 2020.

Abstract: Fossil fuel depletion and aggravation of environmental impacts do not only increase the necessity of bio-refineries but also raise the importance of the sustainability principle. This study adopts a rigorous definition for a sustainable process that is a profitable process that achieves human prosperity and improves the environment by utilizing renewable resources. Bio-refineries may be classified into four platforms; (1) biochemical, (2) thermochemical, (3) biodiesel from jatropha and (4) biodiesel from algae. Such platforms may be in or nearby commercial phase. Process integration is the most effective and methodical way to achieve the objectives of sustainable design. Four different configurations of integration between these platforms are presented in an attempt to generate alternatives in the process design of sustainable bio-refinery.

Keywords: Bio-Refineries, Sustainable Development.

1 Introduction

Energy is one of the most important pillars that supports living evolution. The rise in the standard of living as well as the increase in population sharply increase fossil fuel consumption, which is the main source of energy. For these reasons, the development of alternative fuels is essential. However, such fuels should be feasible technically and economically, environmentally friendly and produced from renewable resources.

Bioenergy produced from biomass contributes 50% of the world's renewable energy [1]. There are various categories and processes of bio-refineries depending on feedstocks [1][2][3]. This research utilizes triglycerides and lignocellulose feedstock only and excludes using starch and sugars feedstocks that impact negatively human food resources. Consequently, biochemical, thermochemical, jatropha and algae become the only four platforms that are in or nearby commercial phase.

The sustainable development principle, raised in the eighties of the last century aiming for environmental protection, has several definitions [4]. This work adopts the more rigorous definition for sustainability: "A sustainable process is one which utilizes renewable resources, improves the environment and is profitable" [5]. Process integration of different bio-refinery platforms is the most methodical way to effectively achieve sustainable design goals [4]. This work presents four different configurations of integration between these platforms.

2 Bio-refineries

The American National Renewable Energy Laboratory (NREL) defines bio-refinery as: "A facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass" [1]. However Maity et al classified bio-refineries based on feedstock into three categories: starch and sugars feedstocks, lignocellulose feedstock and triglycerides feedstock. This paper utilizes triglycerides and lignocellulose feedstocks only and excludes using starch and sugars feedstocks that impact negatively human food resources.

3 Lignocellulose Feedstock

Every year, 10-50 billion dry tons of lignocellulose biomass is produced. Lignocellulose biomass, such as

agriculture wastes and forestry, is considered a sustainable feedstock for biofuel production [6]. It is not only renewable but also decreases greenhouse emissions. Lignocellulose structure is mainly composed of three intersected polymers namely lignin, cellulose, and hemicellulose. Lignin which is a phenolic polymer acts as an envelope that covers the cellulose and hemicellulose which are C₅ and C₆ sugar polymers [7][8]. Biochemical and thermochemical platforms are two the main routes for the production of biofuel from lignocellulose[9].

While there are several routes for a biochemical platform, separate hydrolysis and fermentation are chosen as this provides flexibility in design. Enzymatic hydrolysis is preferred over using acid hydrolysis as it conceptually matches the sustainability principle. This work aims to produce a variety of biofuels and chemicals from lignocellulose, after hydrolysis, which is considered a bottleneck. Simple sugars are split to feed bioethanol fermentation and bioacetone, biobutanol, bioethanol (ABE) fermentation.

As shown in **Figure 1**, Rice straw (lignocellulose) is fractionated using the Organosolv process relying on the recycling of part of the produced bioethanol to remove lignin [7][10][11][12]. While cellulose and hemicellulose are decomposed using enzymatic hydrolysis into their simple sugars [13][14]. These simple sugars are split to feed the traditional bioethanol fermentation using *Z.mobilis* to produce bioethanol and immobilized *C.beijerinckii* ABE fermentation using adsorption as a novel solvent recovery unit which produces bioethanol, biobutanol, and bioacetone [14]–[17].

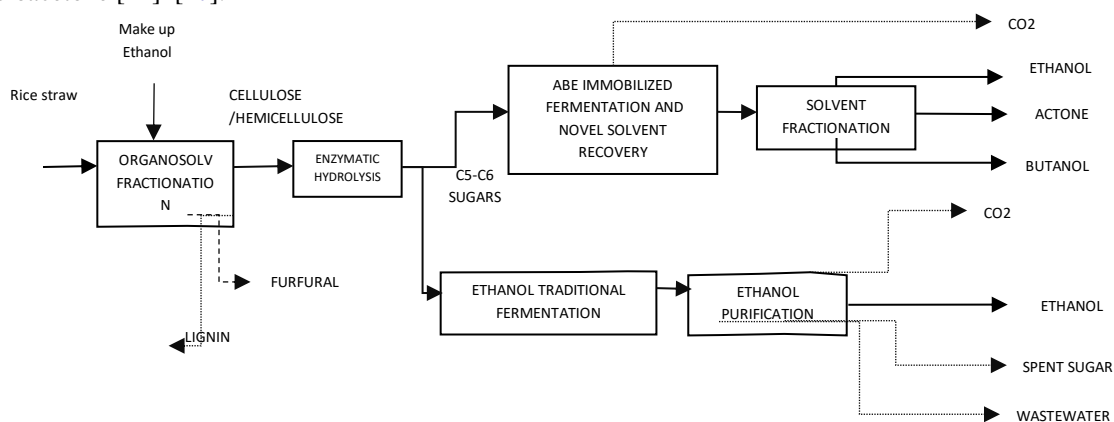


Fig. 1: Biochemical Platform Process Block Diagram.

Material and heat balances for a biochemical platform were developed based on the following data: 100 ton/day of rice straw was fed to Organosolv digester, where 70% of the lignin is dissolved while the lignin recovery reaches 98% by pulp solvent washing[18], 90% of glucan are hydrolyzed into glucose while all C₅ sugars are hydrolyzed to xylose and arabinose in enzymatic hydrolysis [13]. It is assumed that half of the sugars are utilized in ethanol fermentation with 95% conversion of C₆ sugars and 85% of C₅ [13], while 98% of the other half of sugars are converted in ABE fermentation [16]. This platform produces 17.9 ton/day, 10.8 ton/day, 2.3 ton/day, and 3 ton/day of bioethanol, biobutanol, bioacetone, and furfural/HMF respectively. The biochemical standalone platform faces many challenges for sustainability namely; the environmental impacts of the produced carbon dioxide and wastewater which might increase sharply in case of combustion of lignin to generate power and the high cost of the lignocellulose fractionation unit.

Figure 2 shows the thermochemical platform where the biomass is firstly dried then chipped into a smaller size. Syngas is then produced from biomass by a gasifier. The use of an entrained slag gasifier is suitable as it operates at high temperatures near-equilibrium conditions to yield more syngas with high hydrogen content free from hydrocarbons and tar, such as higher-weight organics and oxygenated aromatics that are heavier than benzene [19][20] [21]. The cleaning process targets the removal of any components that might affect the Fischer Tropsch reaction. The selection of the high-temperature gasifier eliminates the need for a tar removal facility, and thus syngas cleaning is confined to quenching to remove particulates (if any) and an amine-based chemical absorber/stripper to remove H₂S and CO₂ [19][21][22]. This syngas needs conditioning to adjust the H₂:CO ratio to meet the requirements of Fischer-Tropsch fuel synthesis process to produce raw fuel which has to be upgraded to convert heavy wax or light gas to yield the required fuel [19][21][22].

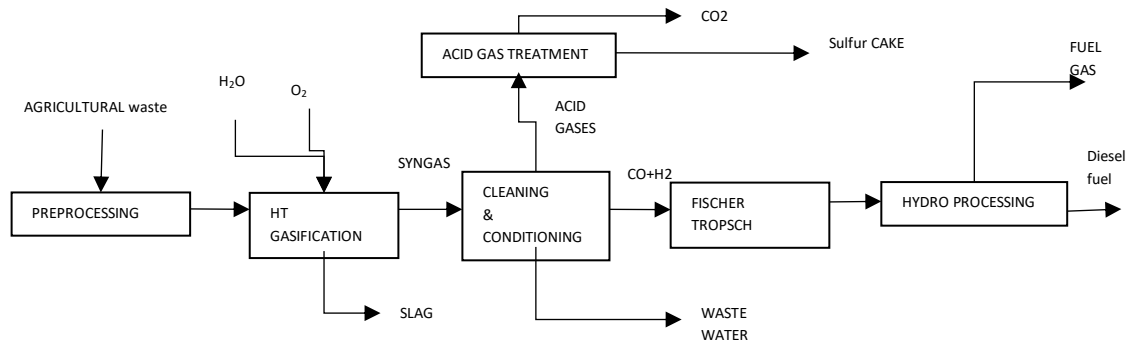


Fig. 2: Thermochemical Platform Process Block Diagram.

The material and heat balances are based on a 100 ton/day biomass for the thermochemical platform depending partially on the data published by the National Renewable Energy Laboratory (NREL) in the technical report prepared by Swanson et al. [19]. The reactions conversions are manipulated to produce syngas with composition and temperature similar to those produced from the HT gasifier in the NREL technical report [19]. The absorber reduces the syngas carbon dioxide and hydrogen sulfide mole fractions to 0.006 % and 0% respectively. The syngas is fed to the Fischer Tropsch reactor which converts carbon monoxide to various paraffinic hydrocarbons using the conversions in the NREL technical report [19]. This platform produces 19.24 ton/day, 1.87 ton/day of diesel and fuel gas respectively. A standalone thermochemical platform defies the sustainability principle as this platform releases a huge amount of CO₂, and generates waste such as wastewater and slag as well as a sulfur cake. The slag is used in road paving, the sulfur cake is used in the fertilizer industry.

4 Triglyceride Feedstock

Vegetable oils, animal fats, waste cooking oils, and micro algal oils are all considered triglyceride (TGD) feedstock sources [1]. Transesterification is the most popular and current method to convert (TGD) to biodiesel [23]. The products obtained from triglycerides such as *Jatropha* oil and algae lipid, are further processed to produce biodiesel [24].

Microalgae are considered the third generation of feedstock used in the production of biofuel. Algae accumulate lipid 7-31 times more than the next best crop. They also have a rapid growth rate compared to terrestrial crops [25][26]. Microalgae has many environmental merits related to their exponential consumption of carbon dioxide. The algae platform shown in **Figure 3** is composed of three main sections; algae cultivation, lipid extraction, and lipid transesterification [26][27]. The photosynthesis-fermentation cultivation model proposed by Miao and Wu is applied in the present work [28]. In this model, cultivation is carried out in two separate stages; an autotrophic stage followed by heterotrophic cultivation. This model can overcome the dualistic challenges of both autotrophic and heterotrophic cultivation. Protothecoide strain, which can be cultivated in both autotrophic and heterotrophic mode, is selected for cultivation [29]. Moreover, the strain has a significant growth rate and yields lipid and biomass [29]. The Sigma™ cultivation system is adopted for photosynthetic autotrophic cultivation [29][30]. This is currently licensed by the Diversified Energy® Corporation (DEC). Algae-cultivation takes place in transparent polyethylene tubes, which permit diffusion of sunlight rays. These tubes are arranged in parallel connected through a manifold to provide equal pressure drop and a steady flow rate. Once the algae cell is separated from the autotrophic clarifier, the heterotrophic cultivation begins as the selected strain can grow in a carbon-rich solvent such as glucose or glycerol in a dark environment. Algae grow in a dark continuous stirred tank reactor (CSTR) known as a fermenter until reaching the specified cell density [26][29].

Lipid recovery is one of the most important milestones that impact the feasibility of biodiesel production from algae lipid. There are two routes for lipid extraction, the first is the traditional route that depends on four main steps which are; dewatering of algae broth from culture followed by harvesting of microalgae from this broth through two main stages, bulk harvesting, and thickening [26][27][31][32][33]. Harvesting is followed by energy-intensive drying, which is pursued by mechanical or solvent lipid extraction. This route has a high energy consumption which impacts the operating cost of the platform. OriginOil™ developed the single-step extraction technology which is based on electromagnetic pulses and micro-bubbles that generate shock waves [29][31][32]. With this new technology, the extraction cost will sharply decrease. Orginoil™ single-step extraction of lipid is then performed followed by lipid transesterification to produce biodiesel and glycerol. A significant portion of the glycerol is recycled to be used as a carbon source in the heterotrophic cultivation step.

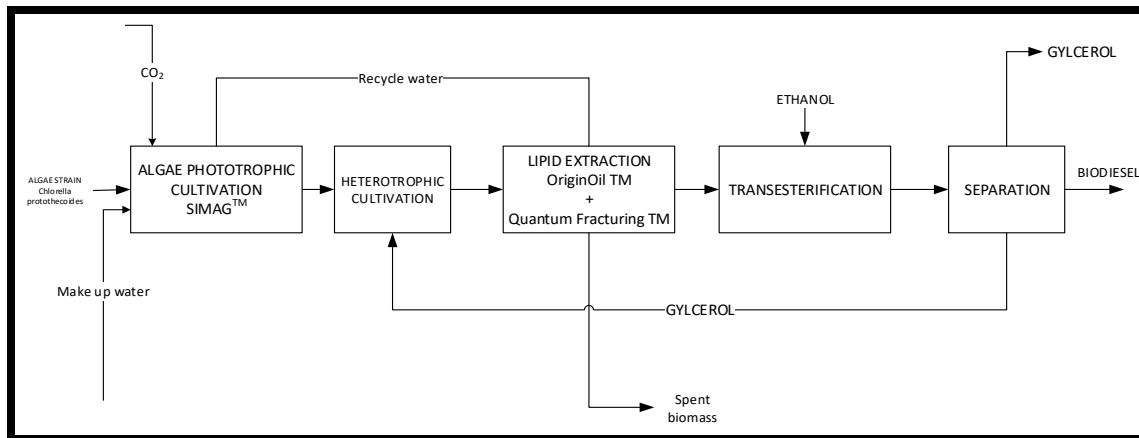


Fig. 3: Algae Platform Process Block Diagram.

The material balance of algae cultivation and lipid extraction sections are based on Choi et al study. This study demonstrates that the production of 1kg of algae biomass requires 1.83 kg of carbon dioxide to achieve a cell density of 2 kg/m³ in the photo bioreactor [34]. Heterotrophic cultivation results in a cell density of 123 kg/m³ and according to Choi et al, lipid recovery is 97% [35]. The material balance of the autotrophic cultivation depends on utilizing all carbon dioxide produced by all of the bio-refinery platforms to achieve the principle of sustainability. As a basis 125 ton/day of carbon dioxide was fed to the algae platform to produce 38.66 ton/day, 3.8 ton/day biodiesel, and glycerol respectively.

Although the algae platform has a high productivity its energy requirement is intensive. The bioethanol used is outsourced and it disposes spent biomass. In the case of using the algae platform standalone scenario, the heterotrophic cultivation depends significantly on produced glycerol as a carbon source. Glycerol is considered a valuable byproduct, which may negatively impact the feasibility of using this platform alone.

The *Jatropha* platform shown in **Figure 4**, commences by farming *Jatropha* fruits followed by seed production through de-hulling and decorticating the fruit and then the oil is mechanically extracted from the seed [36]–[38]. This oil has high FFA which is then treated by pre-esterification [37]. This treated oil is then transesterified to produce biodiesel and glycerol [39].

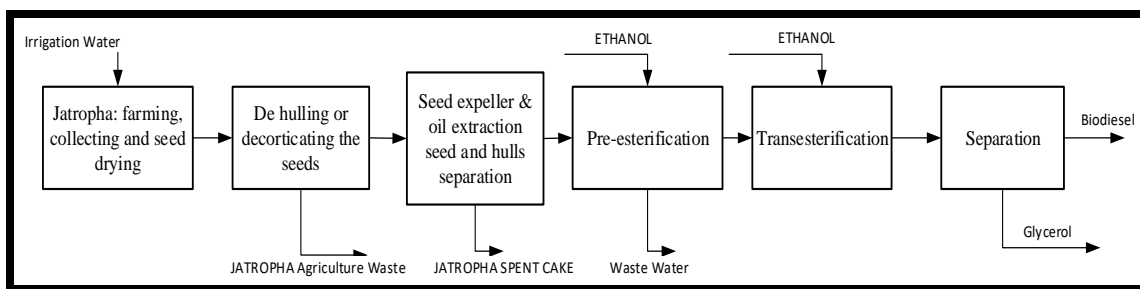


Fig. 4: *Jatropha* Platform Process Block Diagram.

In the *Jatropha* platform, the material mass balance is based on the assumption that 200 feddans are farmed yielding 5 ton seed/feddan annually. The oil represents 40% of the fruit while the remainder is spent biomass [40]. Excess ethanol with 20 mole per mole of FFA is used for the esterification reaction, this will perform 98% conversion of FFA to fatty acid, ethyl ester, and water [41]. This is followed by transesterification to produce biodiesel and glycerol [39]. The *Jatropha* platform produces biodiesel and glycerol daily with capacities of around 1.165 ton/200 feddan and 0.0987 ton/200 feddan respectively.

Jatropha as a standalone platform encounters different challenges as it not only relies on electricity and heat which are sourced from nonrenewable resources (fossil fuel) but also it disposes various agricultural wastes and wastewater which have a negative environmental impact. *Jatropha* as a standalone platform needs bioethanol, which is used in esterification and transesterification.

Biodiesel production through transesterification is divided into two broad categories catalytic and non-catalytic. Catalytic transesterification, whether basic or acidic, is further divided into heterogeneous and homogenous [42]. Both algae lipid and Jatropha oil are transesterified while the latter is pre-esterified to reduce FFA to an acceptable limit for the transesterification process. A transesterification unit is modeled to process algae lipid and treated Jatropha oil to transform these triglycerides to biodiesel. Dow Chemicals has developed Amberlyst which is an acidic ion exchange resin heterogeneous catalyst for the esterification process with direct removal of produced water to forward the reaction in the direction of biodiesel production and reduction of FFA [42]–[45]. This exploits the Esterfip transesterification process, developed by AXENS. This process depends on using a heterogeneous catalyst [45][46]. The transesterification of the pre-esterified Jatropha oil and algae lipid are merged in one process. Excess ethanol, with an ethanol to triglyceride mole ratio of 6, is used depending on the Esterfip process to perform a conversion of 90% of triglyceride to biodiesel and glycerol. Glycerol is decanted in an intermediate step to push the reaction forward to realize 98% conversion [47][48].

5 Sustainability

The largest oil spillage occurred in the waters off California, Santa Barbra in January 1969. This spillage had a significant impact on the environment and marine life which promoted the launch of the concept of sustainability aiming for environmental protection [49][50]. In 1987, the World Commission on Environment and Development defined sustainability as “sustainable development means meeting the needs of the present without compromising the ability of future generations to meet their own needs” [4]. Sikdar et al proposed the US environmental agency definition as “sustainability occurs when we maintain or improve the material and social conditions for human health and the environment over time without exceeding the ecological capabilities that support them”[51]. These definitions spin around achieving the balance between humans, plants, and profit. In other words combining Maximum Production and Minimum Pollution (MPMP) is necessary but not sufficient for sustainability [5]. This work considers that a sustainable process shall improve the environment and that process to go on should rely on renewable resources otherwise this improvement will vanish as the resources are depleted. This work adopts a more rigorous definition for sustainability in which a model of a sustainable process is developed which utilizes renewable resources and results in environmental improvement and profit.

6 Integration

Process integration is defined as a holistic method that achieves the unity of the process that considers optimization of material and energy and reducing environmental impact[52]. Process integration is considered an effective and methodical tool to achieve sustainable processes[4]. One of the integration activities is the generation of alternatives to model and design configurations of sustainable bio-refineries. The present work is a descriptive quantitative study aiming to analyze the integration between the above mentioned four platforms in the following different three scenarios.

- I. Integration between four platforms (innovative integration).
- II. Integration between three platforms.
- III. Integration between two platforms (integrated biorefinery)

This paper will display the configurations screening process for each scenario relying on a sustainable process shall improve the environment, utilizing renewable resources with a commercial technology.

I. Integration between four platforms (innovative integration).

The present work is pioneer research that presents integration between four platforms to generate only one configuration as shown in **Figure 5**. The thermochemical platform disposes of 85 and 20.5 ton/day of carbon dioxide and wastewater respectively while the biochemical platform disposes of 96.3 and 64.1 ton/day. Both carbon dioxide and wastewater are utilized in the cultivation of algae and Jatropha and thus will help in keeping a clean environment and save water. 31.4 ton/day of lignin as well as 4.56 ton /day of Jatropha cake form a combined waste which is fed to the thermochemical platform. The thermochemical platform is flexibly designed to accept different feedstock. This provides a potential for using chemically produced lignin and thus secure a stable feed and avoiding total shut down. Spent algae cells, which do not contain lignin [53], are easily hydrolyzed to protein and mixed sugars. 44.6 ton/day of these mixed sugars are fed to the fermentation step in the biochemical platform, which ensures the operation of the bioethanol distillation and ABE columns to increase the productivity of chemicals and fuels such as bioacetone, biobutanol, and bioethanol. Spent waste sugars from the fermentation step in the biochemical platform are used as a carbon source for the algae heterotrophic cultivation. Transesterification of both algae lipid and low FFA Jatropha oil in one process unit decreases the capital cost and enhances project economics. After the reduction of its FFA in a pre-esterification unit, 1.58 ton/day of low FFA Jatropha oil is directed to the algae platform where it is transesterified commonly with algae lipid. Bioethanol required for pre-

esterification and transesterification is split from the bioethanol stream produced in the biochemical platform. The thermochemical platform supplies the power required for heating and electricity for the operation of the whole integrated bio-refinery.

The 4 platforms integrated bio-refinery produces various fuels and chemicals. It produces; diesel, biodiesel which is mixed with diesel, bioethanol, and biobutanol which have the potential to be blended with gasoline in addition to several chemicals such as bioacetone, glycerol, and furfural as well as solid products like elemental sulfur and slag. Sulfur is used as a feedstock for different industries such as fertilizers while slag is used in road paving.

Other approaches suggest switching between Jatropha cakes as the biochemical platform feed while algae spent biomass is fed to the thermochemical platform. This approach is not logically accepted as it loses significant merit that algae spent biomass is distinguished by lack of lignin and is easily hydrolyzed to protein and mixed sugars for the biochemical platform [26][53].

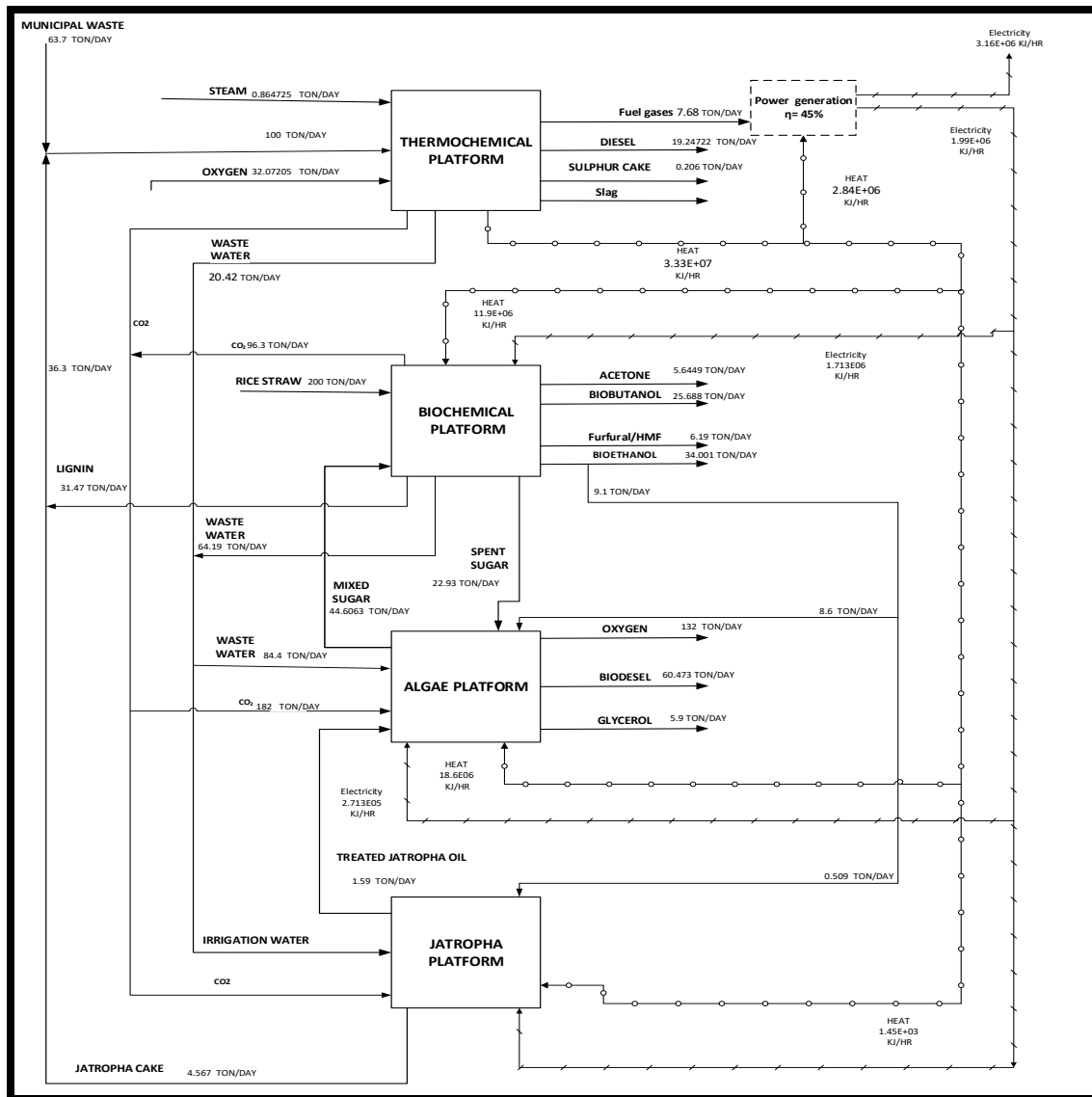


Fig. 5: Integration between Four Platforms.

II. Integration between three platforms.

The Jatropha platform depends on the cultivation of 200 acres to produce 1.59 tons/day of biodiesel. This throughput is limited compared to the algae platform, which produces around 60 tons/day of biodiesel. Besides, the Jatropha platform consumes heat and electricity. Owing to the above-mentioned reasons excluding the Jatropha platform from the biorefinery configuration is considered for cost reduction. Although this exclusion has little

impact on the material and heat balance previously performed for the four integrated platforms, however, due to the shortage of the Jatropha spent cake, the flow rate of the municipal waste is increased to keep the same flow rate to the thermochemical platform.

The produced bioethanol was found to increase by 0.5 ton/day, which is used in pre-esterification. The overall throughput when compared to the 1st configuration, shown in **Figure 6**, reveals that the municipal waste increases by 4.8 ton/day while the production rate of the biodiesel and glycerol decreases by 0.543 and 0.07 ton/day respectively when compared to the flow rates of 1st configuration. On the other hand, bioethanol production increases by 0.51 ton/day and production of electricity increases by more than 0.01 kJ/hr.

While this work display “Thermochemical-Biochemical-Algae” (TBA) integration as a sustainable configuration, there are other three alternatives of integration that do not match this work sustainability approach for instance: “Thermochemical-Biochemical-Jatropha” (TBJ) integration and “Biochemical-Jatropha- Algae” (BJA) integration. The former alternative disposes of carbon dioxide and wastewater to the environment, the Jatropha platform has limited ability compared to the algae platform to absorb carbon dioxide and wastewater produced from the biochemical and thermochemical platforms. The latter alternative in the absence of a thermochemical platform is considered as a source of power, will depend on non-renewable resources is not inconsistent with a sustainable definition.

However the third alternative “Thermochemical-Jatropha- Algae” (TJA) integration does not contradict with sustainable definition, unfortunately, this work does not study this configuration. As mentioned above, Jatropha throughput is limited compared to the algae platform so the material balance of this configuration will resemble that of “Thermochemical- Algae” (TA).

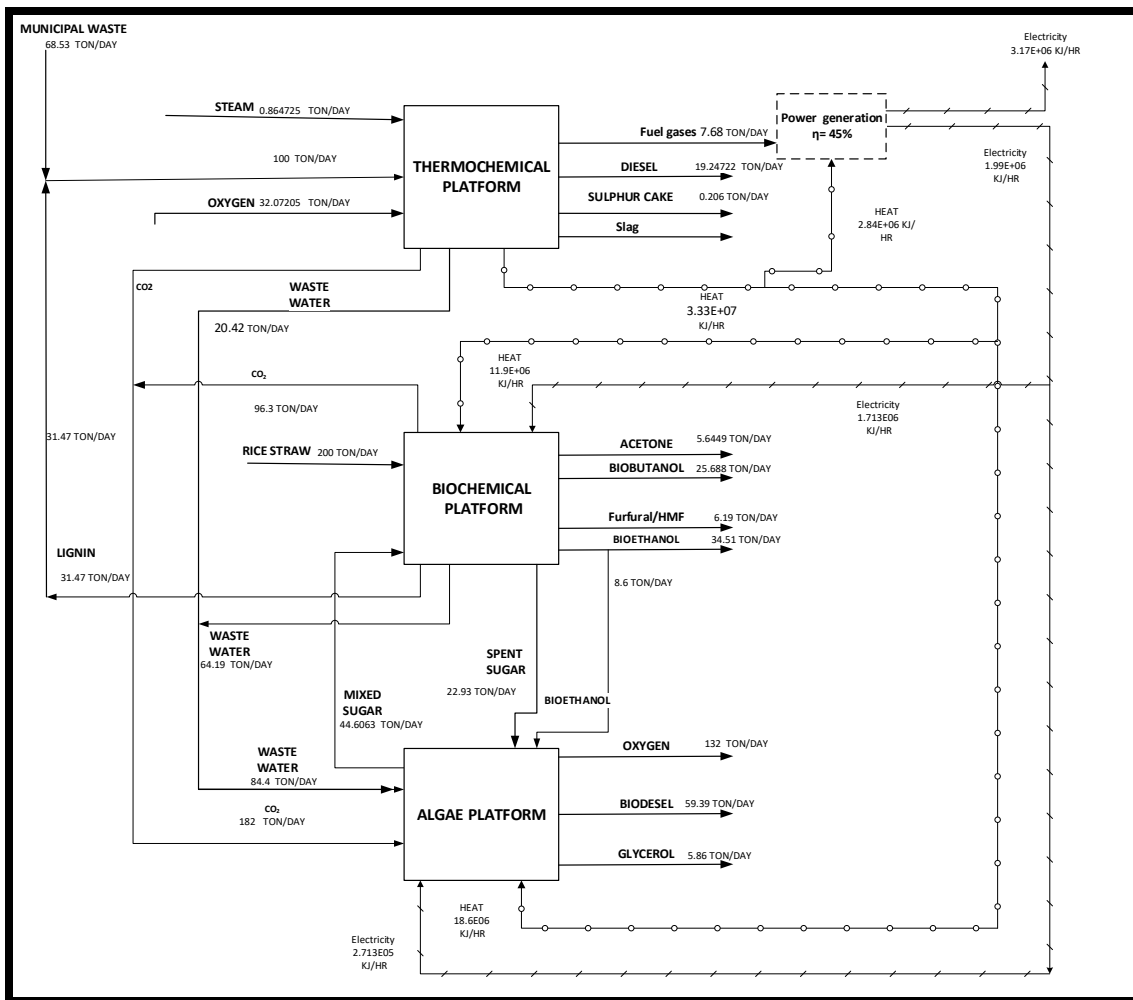


Fig.6: Integration between Three Platforms.

III. Integration between two platforms (integrated biorefinery)

Six available configurations represent integration between two platforms, but only two of these configurations match this work's sustainable objectives. The configuration formed from classical “thermochemical-biochemical” (TB) integration, discerned that this integration with this process synthesis faces a significant challenge to achieve sustainability. This configuration produces a huge quantity of carbon dioxide in addition to wastewater and unutilized spent sugars, which are considered a waste.

“Thermochemical-Jatropha”(TJ) integration from one side or “biochemical-Jatropha”(BJ) from the other side do not coincide with this work sustainability rigorous definition. Jatropha platform has limited ability to absorb carbon dioxide and wastewater either produced from the biochemical or thermochemical platform. “Algae -Jatropha” (AJ) integration is the fourth configuration that does not match with this work as this configuration lacks a renewable power source. It will depend on non-renewable resources, which is inconsistent with a sustainable definition. This work proposes “Thermochemical-Algae” (TA) integration and “Biochemical- Algae” (BA) integration as two alternatives of integration between two platforms

Thermochemical- Algae Platform Integration

As presented in **Figure 7**, carbon dioxide and wastewater, with capacities of 85.3 and 20.42 ton/day respectively, are transferred from the thermochemical to the algae platform to be utilized in cultivation, while the algae spent biomass, from lipid extraction section, is used as a feedstock for the thermochemical platform. Heterotrophic algae cultivation relies on by-product glycerol. The thermochemical platform supplies power to both platforms and excess produced power is used for the production of electricity to be used elsewhere.

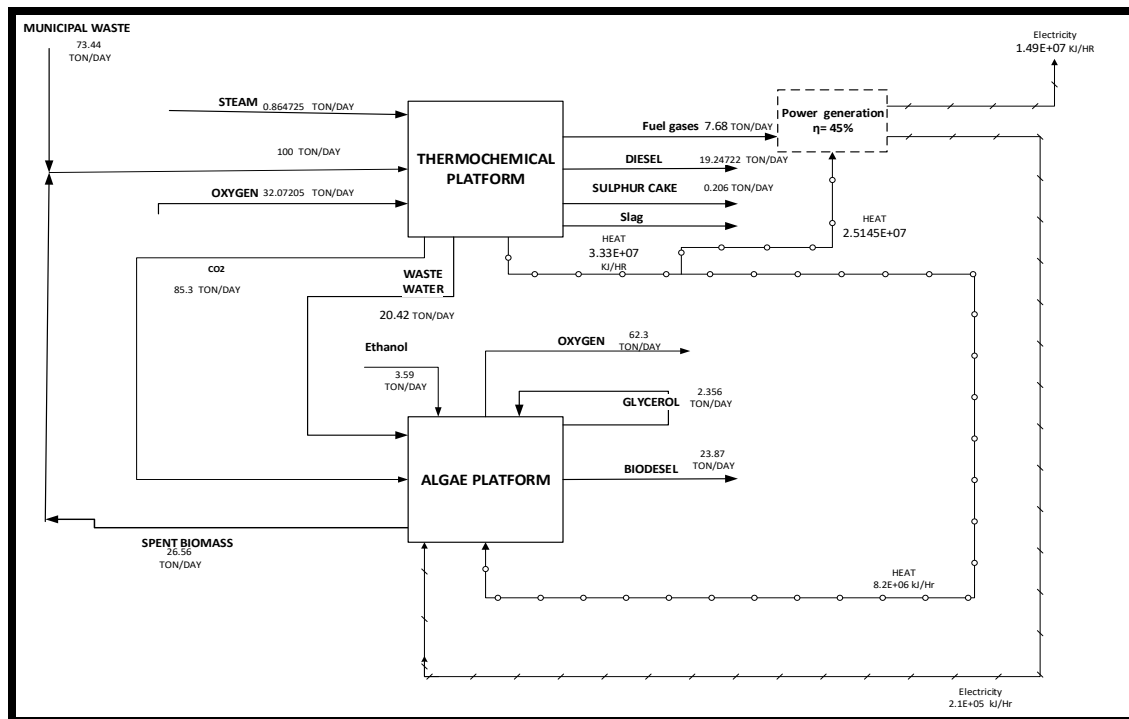


Fig.7: Thermochemical-Algae Platform Integration.

Bioethanol used in the transesterification of algae lipids to produce biodiesel is outsourced. The algae platform throughput is reduced due to the lack of mixed sugars. Heterotrophic cultivation is controlled with recycled glycerol. This environment friendly configuration produces 62.3 tons/day of oxygen. The main products of this configuration are diesel and biodiesel with capacities of 19.42 and 23.8 ton/day respectively. Although this configuration produces limited products, it is the highest with respect to the production of excess electricity as it produces 1.49 E07 kJ/hr.

Biochemical - Algae Platform Integration

The integration between the Biochemical and Algae platforms is presented in **Figure 8**, the only problem that hinders the use of this configuration is the source of heat and electricity. This problem could be solved by the

addition of a power generation unit from lignin combustion. The produced power is used in operating the whole configuration.

The carbon dioxide from power generation and the biochemical platform is directed to the algae platform and is used in autotrophic cultivation in addition to wastewater, which is used in algae cultivation. Spent sugars from the fermentation are used in the algae heterotrophic cultivation, while algae spent biomass is easily hydrolyzed to form mixed sugars, which are used as feed to the fermentation process to increase productivity and keep the operation of distillation columns in downstream of fermentation if there is any shortage of rice straw. 9.4 ton /day is split from the bioethanol stream product to be used in the transesterification of algae lipid to biodiesel.

This model relies on adding a new power generation unit for supplying the required power in the absence of the thermochemical platform. This model has the lowest capital cost among all studied three and four integrated platforms due to the absence of the thermochemical platform with its high number of equipment. However, this model lacks flexibility for a future extension for utilizing of lignin in the manufacturing of chemicals.

This configuration consumes more rice straw, around 225 ton/day, than the previous configurations, to provide sufficient lignin for power generation. Although this configuration produces various products such as oxygen, bioacetone, biobutanol, bioethanol, biodiesel, and glycerol, it is considered the lowest in power generation.

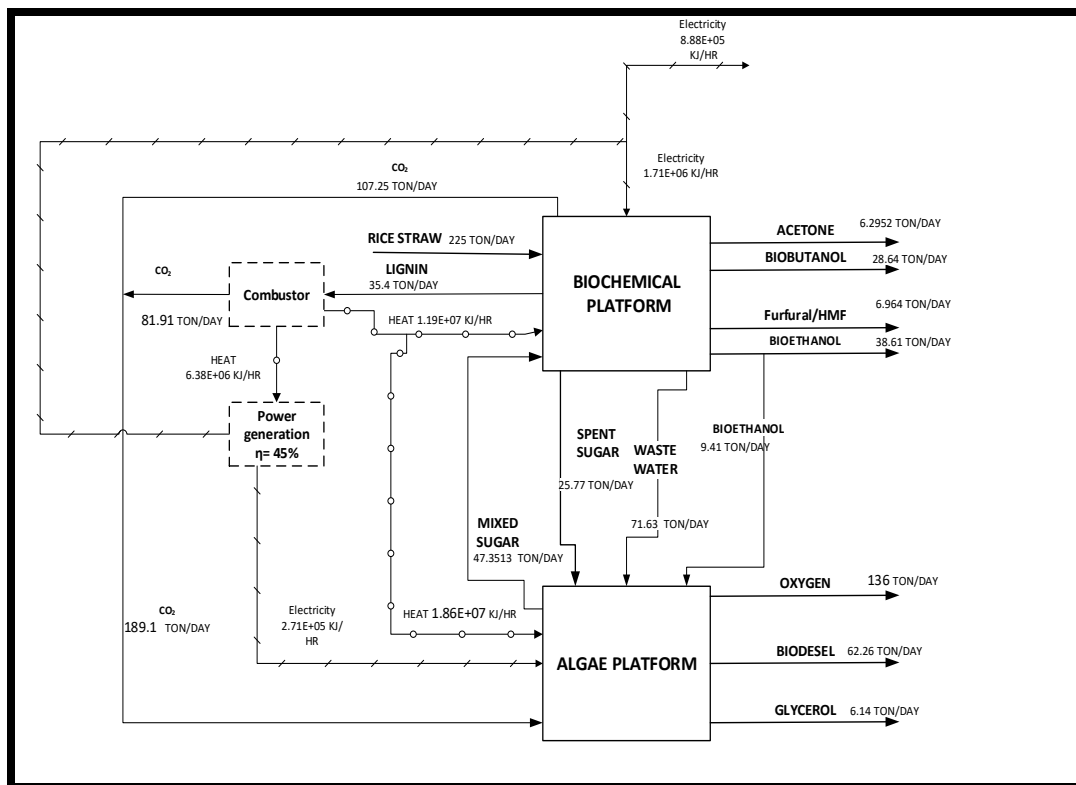


Fig.8: Biochemical-Algae Platform Integration

7 Conclusion and Further Perspectives

This study concluded the following:

- It is quite difficult for standalone Biochemical platform, Thermochemical platform, jatropha platform and algae platform to achieve sustainability with its rigorous definition.
- Four different configurations of integration between these platforms are presented in an attempt to generate alternatives in the process design of sustainable bio-refinery.
- The Thermochemical platform is considered as a source of power for the whole integrated bio-refinery. In its absence, adding a power generation unit is mandatory.
- The algae platform play a main role in achieving sustainability due to its potential to utilize carbon dioxide and wastewater disposed by other platforms.

- The integration between four platforms produces various products, has the highest capital cost due to the necessity of a large number of equipment in addition to the need for cultivation of 200 faddan of *Jatropha*.
- Although the integration between Thermochemical-Algae platforms has limited products such (diesel, biodiesel and glycerol), however it produces the highest amount of electricity compared to other configurations.
- The integration between Biochemical-Algae platforms produces various products with the lowest electrical power consumption.

References

- [1] S. K. Maity, "Opportunities, recent trends and challenges of integrated biorefinery: Part I," *Renew. Sustain. Energy Rev.*, **43**, 1446–1466, 2015.
- [2] A. Singh, S. I. Olsen, and P. S. Nigam, "A viable technology to generate third-generation biofuel," *J. Chem. Technol. Biotechnol.*, **86(11)**, 1349–1353, 2011.
- [3] A. Singh and P. Nigam, "Microbial biofuels production," *Microb. Biotechnol.*, (**June 2016**), 155–168, 2014.
- [4] M. M. El-Halwagi, *Sustainable Design Through Process Integration: Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement*. Oxford, UK: Elsevier., 2012.
- [5] S. Elnashaie, "Environmental Engineering and Sustainable Development," *Int. Conf. Chem. Environ. Eng.*, **9(6)**, 413–439, 2018.
- [6] H. Chen, *Lignocellulose biorefinery feedstock engineering Principles and Applications*. Woodhead Publishing Limited is an imprint of Elsevier., 2015.
- [7] S. H. (1985) E. Chum HL, Douglas LJ, Feinberg DA, "Evaluation of pretreatment in enzymatic hydrolysis of cellulose," 1985.
- [8] V. T. S. and C. R. S. Adenise Lorenci Woiciechowski, Luciana Porto de Souza Vandenberghe, Susan Grace Karp, Luiz Alberto Junior Letti, Júlio Cesar de Carvalho, Adriane Bianchi Pedroni Medeiros, Michele Rigon Spier, Vincenza Faraco, "Chapter 3 The Pretreatment Step in Lignocellulosic Biomass Conversion: Current Systems and New Biological Systems," in *Lignocellulose Conversion.*, 2013.
- [9] J.-L. W. and O. Bédoué, *Lignocellulosic Biorefineries*. EPFL Press, 2013.
- [10] Xuebing Zhao & Keke Cheng & Dehua Liu, "Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis," *Appl. Microbiol. Biotechnol.* · March 2009, no. September 2016, 2009.
- [11] J. Hagman, L. Hedborn, M. Isgren, and P. Mårtensson, "Comparison of pretreatments for ethanol production from softwood," 2012.
- [12] N. V. Ortiz, DAlex BERLIN, Burnaby (CA); Mikhail Y. BALAKSHIN, D. (CA); Raymond M A' Burnaby (CA); Vera MAXIMENKO GUTMAN, Igéigaby (CA); Darwin ORTIZ, and (73)arwin, "ORGANOSOLV PROCESS," 2013.
- [13] D. Humbird et al., "Process design and economics for conversion of lignocellulosic biomass to ethanol," 2011.
- [14] C. HA. Dutta, M. Talmadge, and J. Hensley National Renewable Energy Laboratory Golden, W. M. Worley and D. Dudgeon Harris Group Inc. Atlanta, Georgia and Seattle, M. D. Barton, P. Groenendijk, D. Ferrari, and B. Stears The Dow Chemical Company Midland, I. E.M. Searcy, C.T. Wright, and J.R. Hess Idaho National Laboratory Idaho Falls, and Prepared, "Process design and economics for conversion of lignocellulosic biomass to ethanol," 2011.
- [15] C. Xue, J. Zhao, and L. Chen, "Integrated butanol recovery for an advanced biofuel : current state and prospects," *Appl Microbiol Biotechnol*, 2014.
- [16] N. Abdehagh, F. H. Tezel, and J. Thibault, "Separation techniques in butanol production: Challenges and developments," *Biomass and Bioenergy.*, **60**, 222–246, 2014.
- [17] A. B. Van Der Merwe, H. Cheng, J. F. Görgens, and J. H. Knoetze, "Comparison of energy efficiency and economics of process designs for biobutanol production from sugarcane molasses," *Fuel.*, **105**, 451–458, 2013.
- [18] J. Kautto, M. J. Realff, and A. J. Ragauskas, "Design and simulation of an organosolv process for bioethanol production," *Biomass Convers. Biorefinery.*, **3**, 199–212, 2013.
- [19] R. M. Swanson, J. a Satrio, R. C. Brown, and D. D. Hsu, "Techno-Economic Analysis of Biofuels Production Based on Gasification Techno-Economic Analysis of Biofuels Production Based on Gasification Alexandru Platon," 2010.

- [20] P. Basu, Biomass gasification, pyrolysis and torrefaction: Practical design and theory, 2nd editio. Saint Louis, MO, USA: Academic Press. Retrieved from, 2018.
- [21] J. C. and J. C. Rafael Luque, Handbook of Biofuels Production Processes and technologies. Woodhead Publishing Limited., 2011.
- [22] A. de Klerk., "Synthesis Gas Production, Cleaning, and Conditioning," in Fischer-Tropsch Refining, Arno de Klerk, Ed. Wiley-VCH., 2011.
- [23] M. Ahmad, M. Khan, M. Zafar, and S. Sultana, Practical Handbook on Biodiesel Production and Properties, vol. 20121030. CRC Press., 2012.
- [24] A. Sarin, Biodiesel Production and Properties. The Royal Society of Chemistry, 2012.
- [25] T. Demirbas, M. Fatih Sila Science, University Mahallesi, Mekan Sokak No. 24, Trabzon, "Biofuels from algae for sustainable development," *Appl. Energy.*, **88(10)**, 3473–3480, 2011.
- [26] H. M. A. A. Catarina Guede, "Applications of Spent Biomass," in Biofuels from Algae, Elsevier Ltd., 1–338, 2013.
- [27] D. D. Das Das and D. of B. I. I. of T. Kharagpur, Algal Biorenew: An Integrated Approach. Co-published by Springer International Publishing, Cham, Switzerland, with Capital Publishing Company, New Delhi, India., 2015.
- [28] W. Xiong, C. Gao, D. Yan, C. Wu, and Q. Wu, "Double CO₂ fixation in photosynthesis-fermentation model enhances algal lipid synthesis for biodiesel production," *Bioresour. Technol.*, **101(7)**, 2287–2293, 2010.
- [29] D. Choi, S. Glantz, and J. I. Al Sous, "Algae to biodiesel," Pennsylvania, 2011.
- [30] G. B. Cloud and A. Z. Us, "PRESSURIZED FLEXIBLE TUBING SYSTEM FOR PRODUCING ALGAE," US 2008/0311649 A1, 2008.
- [31] W. Chan and P. M. Schenk, "Minireview Progress on lipid extraction from wet algal biomass for biodiesel production," 2016.
- [32] J. J. M. and S. Heaven, "A Review of the Harvesting of Micro-algae for Biofuel Production John.," 1–28, 2013.
- [33] E. Günerken, E. D. Hondt, M. H. M. Eppink, L. Garcia-gonzalez, K. Elst, and R. H. Wijffels, "Cell disruption for microalgae biorefineries," *Biotechnol. Adv.*, 2015.
- [34] D. Choi, S. Glantz, and J. I. Al Sous, "Algae to biodiesel," Pennsylvania., 2011.
- [35] D. Choi, S. Glantz, and J. I. Al Sous, "Algae to biodiesel," *ScholarlyCommons*, vol. Senior Des., 2011.
- [36] B. Yuan, R. Shamsudin, B. T. H. Tuah, and R. Yunus, "A review of processing and machinery for *Jatropha curcas* L. fruits and seeds in biodiesel production: Harvesting, shelling, pretreatment and storage," *Renew. Sustain. Energy Rev.*, **52**, 991–1002, 2015.
- [37] N. Carels, M. Sujatha, and B. Bahadur, *Jatropha*, challenges for a new energy crop: Volume 1: Farming, economics and biofuel. Springer Berlin Heidelberg., 2012.
- [38] W. M. J. Achten et al., "Jatropha bio-diesel production and use," *Biomass and Bioenergy.*, **32(12)**, 1063–1084, 2008.
- [39] A. Demirbas, "Comparison of transesterification methods for production of biodiesel from vegetable oils and fats," *Energy Convers. Manag.*, **49(1)**, 125–130, 2008.
- [40] B. Y. Lim, R. Shamsudin, B. T. H. T. Baharudin, and R. Yunus, "A review of processing and machinery for *Jatropha curcas* L. fruits and seeds in biodiesel production: Harvesting, shelling, pretreatment and storage," *Renew. Sustain. Energy Rev.*, **52**, 991–1002, 2015.
- [41] WULF DIETRICH, L. MLECZKO, and HEINRICHMORHENN, "PROCESS FOR HETEROGENEOUSLY CATALYSED ESTERIFICATION OF FATTY ACIDS," US 2009/0294358 A1, 2009.
- [42] E. F. Aransiola, T. V. Ojumu, O. O. Oyekola, T. F. Madzimbamuto, and D. I. O. Ikhu-Omoregbe, "A review of current technology for biodiesel production: State of the art," *Biomass and Bioenergy.*, **61**, 276–297, 2014.
- [43] D. C. Kannan, "a Solid Catalyst Method for Biodiesel Production," 2009.
- [44] O. Thum and L. Hilterhaus, "PROCESS FOR HETEROGENEOUSLY CATALYSED PREPARATION OF CARBOXYLIC ACID DERIVATIVES," US Pat. App. 12/354,256, vol. 1, no. 19, 2009.
- [45] R. Luque and J. A. Melero, *Advances in biodiesel production*. 2012.
- [46] W. Bacovsky, Dina Körbitz Körbitz, "BIODIESEL PRODUCTION: TECHNOLOGIES AND EUROPEAN PROVIDERS REPORT TO IEA BIOENERGY TASK 39," 2007.
- [47] A. Talebian-Kiakalaieh, N. A. S. Amin, and H. Mazaheri, "A review on novel processes of biodiesel production from

- waste cooking oil,” *Appl. Energy.*, **104**, 683–710, 2013.
- [48] V. COUPARD, S. Maury, and V. Pugno, “PROCESS FOR PREPARING ESTERS OF ALCOHOLS AND GLYCERIN FROM TRIGLYCERIDES AND ALCOHOLS USING A HETEROGENEOUS CATALYST IN THE PRESENCE OF A CONTROLLED QUANTITY OF WATER,” US 2011/0065942 A1, 2011.
- [49] Jeremy Caradonna, *Sustainability—History*. Oxford University Press, 2014.
- [50] U. S. A. John Lemons(Department of Life Sciences, University of New England, Biddeford, ME, U. S. A. . Donald A. Brown (Bureau of Hazardous Sites and Superfund Enforcement, Pennsylvania Department of Environmental Resources, Harrisburg, PA, and Spri, *Sustainable Development: Science, Ethics, and Public Policy*. 5 Springer Science+Business Media Dordrech, 1395.
- [51] S. K. Sikdar, “Sustainability Development and Sustainability Metrics,” *AIChE J.*, **49(8)**, 25, 2003.
- [52] M. M. El-Halwagi, *Process Integration*, vol. 7. Elsevier B.V., 2006.
- [53] V. K. Eduardo Sánchez-Tuirán, Mahmoud M. El-Halwagi and Section, “Integrated Utilization of Algae Biomass in a Biorefinery Based on a Biochemical Processing Platform,” in *Integrated Biorefineries DESIGN, ANALYSIS, AND OPTIMIZATION*, CRC Press Taylor & Francis Group., 874, 2012.