Preprints of the 10th IFAC International Symposium on Dynamics and Control of Process Systems
The International Federation of Automatic Control
December 18-20, 2013. Mumbai, India

Superstructure optimization of biodiesel production from microalgal biomass

Muhammad Rizwan*, Jay H. Lee,**
Rafiqul Gani***

**Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea (Tel: 0082-42-350-3966; e-mail: mrizwan@kaist.ac.kr).*
***Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Republic of Korea (e-mail: jayhlee@kaist.ac.kr)*
**** CAPEC, Department of Chemical and Biochemical Engineering. Technical University of Denmark, Dk-2800 Kgs Lyngby, Denmark (e-mail: rag@kt.dtu.dk)*

Abstract: In this study, we propose a mixed integer nonlinear programming (MINLP) model for superstructure based optimization of biodiesel production from microalgal biomass. The proposed superstructure includes a number of major processing steps for the production of biodiesel from microalgal biomass, such as harvesting of microalgal biomass, pretreatments including drying and cell disruption of harvested biomass, lipid extraction, transesterification, and post-transesterfication purification. The proposed model is used to find the optimal processing pathway among the large number of potential pathways that exist for the production of biodiesel from microalgae. The proposed methodology is tested by implementing on a specific case study. The MINLP model is implemented and solved in GAMS using a database built in Excel. The results from the optimization are analyzed and their significances are discussed.

Keywords: Biodiesel, microalgae, superstructure optimization, mixed integer nonlinear programming, biorefinery

1. INTRODUCTION

Development of sustainable fuels production from biomass has become very important due to the increased concerns for the greenhouse gas emissions, dwindling fossil fuel reserves, and unstable prices of petroleum fuels. Biofuels produce less net amounts of carbon dioxide than fossil fuels and by utilizing them as transportation fuels and other energy sources, the level of carbon dioxide in the atmosphere may be reduced. Among the various potential routes for the production of biodiesel, the transesterification of vegetable oils is the best known and is currently commercialized. However, due to their competition with food market, this route is not viewed as being sustainable, certainly not at a scale that can alleviate the global warming. Microalgae has been touted as a promising feedstock for the production of biofuels since it grows fast, has high oil contents, and is a non-food feedstock.

Microalgae can serve as feedstock for a wide range of products due to its high quantity of natural lipids, proteins, carbohydrates, vitamins, pigments and enzymes (Harun et al. 2010). The processing methods used for producing biofuels and other valuable products from microalgae fall under the broad concept of biorefinery. The term biorefinery is coined to describe the production of a wide range of biofuels and chemicals from biomass through the integration of bioprocessing and appropriate low environmental impact chemical technologies in a cost-effective and environmentally sustainable manner (Li et al. 2008). Conceptually, a micro-algae feedstock based biorefinery would involve sequentially the cultivation of microalgae in a microalgal farming facility (CO2 mitigation), extraction of bioreactive products from harvested algal biomass, thermochemical processing, biochemical processing, extraction of high value chemicals, and reforming/upgrading of the biofuels for different applications (Li et al. 2008). The concept of algal biomass biorefinery can assist in making biofuel production economically viable (Gouveia, 2011). An algal biorefinery could and should integrate several different conversion technologies.

Ragauskas et al. (2006) demonstrated the roadmap for the research for biorefineries in the 21st century. A possible way to advance the state of the art is through a systematic design of biorefinery (Lynd et al. 1999). Energy systems engineering can be used to synthesize the promising biorefinery configurations and to find economically promising processing routes for the production of biofuels (Liu et al. 2009).

A systematic framework for the synthesis and design of optimal processing networks is presented in many studies (Grossman 1990; Yeomans and Grossman 1999). These studies provide a basis for using the mathematical programming approach to solve the processing networks problems and to determine the optimal processing route. Zondervan et al. (2011) formulated a superstructure based optimization model to find the optimal processing network for the production of five products (ethanol, butanol, succinic acid, gasoline and gasohol) from two types of feed stocks (lignocellulosic biomass and crude oil). The proposed approach in their study united the trans-shipment model with a superstructure, resulting in a MINLP problem. Quaglia et al. (2012) proposed an integrated business and engineering framework for synthesis and design of processing networks.

The process network design/synthesis problem is defined as a MINLP problem. The developed framework was applied to an industrial case study to find the optimal processing network for the utilization of a resource (soybean oil) from the soybean oil industry under four different scenarios.

In this study, we propose a processing network model representing the potential processing pathways for the production of biodiesel from microalgal biomass. A superstructure based optimization model has been formulated and the problem of finding the optimal processing pathway under a chosen objective is formulated as a MINLP problem. The MINLP problem is formulated and solved in the software package GAMS with a database built in Excel.

2. METHODOLOGY

2.1 Problem Definition

Given a superstructure composed of available options for the various processing steps (harvesting of microalgal biomass, pre-treatment step including drying and cell disruption of harvested biomass, lipid extraction, transesterification, and post-transesterfication purification), the optimization problem is defined as: Determine the optimal processing route for the production of desired product, biodiesel, from the specified raw material, microalgal biomass. The objective function for the optimization is chosen as the maximization of the yield of the desired product but it can also include other objectives such as the minimization of the processing costs (the cost of the raw materials, utilities and chemicals) and/or the amount of waste products.

2.2 Development of Superstructure

All potential alternatives in the processing network are represented by a particular schematic form, which is called the superstructure (Grossmann 1990). Hence, the superstructure contains all candidates for feasible and optimal processing pathways. In formulating the superstructure, all the potential raw materials and products are specified and then linked through a series of tasks (unit operations and/or unit processes) such that the raw materials get converted into the products. An example of a task can be mixing, separation, reaction, etc.

We have developed a superstructure model for the production of biodiesel from microalgal biomass (shown in Fig. 1) based on the data taken from published literature. It consists of five major processing steps/stages: (1) harvesting of microalgal biomass, (2) pre-treatment step including drying and cell disruption of harvested biomass, (3) lipid extraction, (4) transesterification, and (5) post-transesterfication purification. Each processing stage has several options/technological alternatives to perform the respective task. Each option/technological alternative included in the superstructure is represented by two indices; the first index represents the option/technological alternative and the subsequent second index represents the processing step/stage. For example the index '1,2' represents the first option in the second processing stage. Physical descriptions for all the options in the superstructure model are given in Table 1.

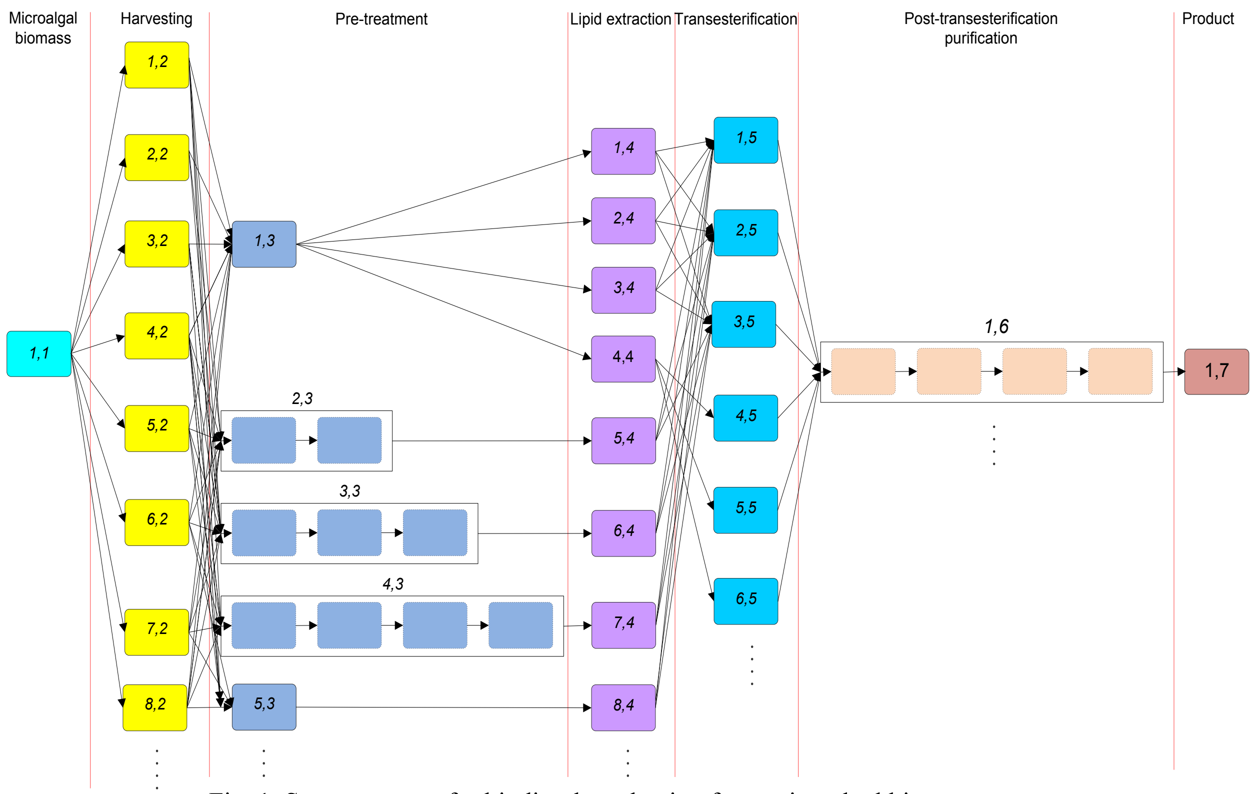

Fig. 1. Superstructure for biodiesel production from microalgal biomass

As shown in Fig. 1:

- Eight technological alternatives are included in the superstructure for carrying out the harvesting of microalgal biomass.

- Four alternatives are considered for pre-treatment of harvested biomass, each involving different number of processing units. The fifth option (5,3) represents the bypassing of the pre-treatment step, which may be appropriate when the lipids are extracted directly from wet microalgal biomass.

- Seven alternatives are included for the lipid extraction step. The fourth option of this stage (4,4) is used to bypass the lipid extraction entirely to accommodate in-situ transesterification in the subsequent stage.

- Six alternatives are included for performing the transesterification, including the three alternatives to perform in-site transesterification.

- In the post-transesterification purification stage, only one option is considered. Therefore, no decision is involved for this stage.

Note that as the technology for microalgal based biodiesel production evolves, more options will be created, which can be incorporated into the superstructure.

Table 1. List of technological alternatives/options

1,1	Microalgal biomass
1,2	Flocculation with polyelectrolyte
2,2	Flocculation with sodium hydroxide
3,2	Flocculation with polyaluminium chloride
4,2	Flocculation with aluminium sulphate
5,2	Flocculation with chitosan
6,2	Flocculation with poly ϒ-glutamic acid
7,2	Centrifugation
8,2	Filtration
1,3	Drying
2,3	Drying + Grinding
3,3	Drying + Grinding + Microwave
4,3	Drying + Grinding + Microwave + Ultrasonication
5,3	Empty
1,4	Solvent extraction
2,4	Solvent extraction with soxhlet apparatus
3,4	Supercritical fluid extraction
4,4	Empty
5,4	Grinding-assisted solvent extraction
6,4	Microwave-assisted solvent extraction
7,4	Ultrasound-assisted solvent extraction
8,4	Lipid extraction from wet microalgal biomass
1,5	Base-catalysed transesterification
2,5	Acid-catalysed transesterification
3,5	Enzyme-catalysed transesterification
4,5	Alkaline in-situ transesterification (including lipid extraction)
5,5	Acidic in-situ transesterification (including lipid extraction)
6,5	Enzymatic in-situ transesterification (including lipid extraction)
1,6	Methanol recovery by distillation + Gravity separation + Washing of biodiesel + Purification of biodiesel by distillation
1,7	Biodiesel

2.3 Modelling

2.3.1 Mass Balance Constraints

Mass balances must be satisfied at each processing stage. In the generic form of the model, the mass balance at option *k* of stage *j* is modelled through equations (1) – (10). A general flow diagram for a processing stage and that for each technological alternative/option within a stage are given by the illustrations in Fig. 2(a) and (b) respectively.

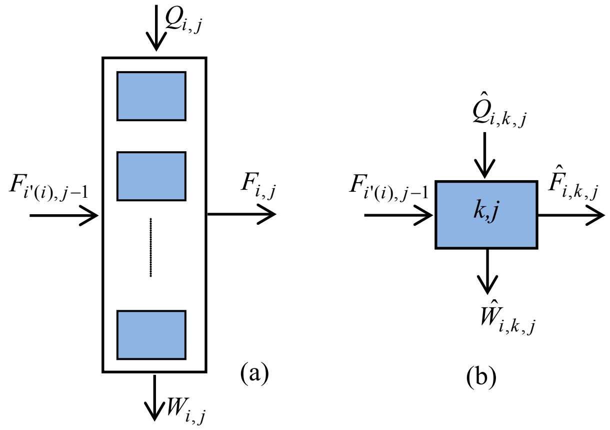

Fig. 2. Representation of (a) processing stage *j*, (b) option *k* in stage *j*

Before we go any further, some explanations regarding the nomenclature is in order. The nomenclature is given in Fig 2. Indices appearing as subscripts are explained in Table 2. One notable point is that these indices are arranged such that later appearing indices determine the range of earlier appearing ones. For example, in $F_{i,j}$, the range of component index *i* is dependent on the stage index *j*, *i.e.,* for each *j*, there is a specific range for *i*, which indexes the components that are relevant to that stage. Since the component lists for different stages may vary, in order to avoid confusion, the notation $F_{i',j-1}$ is used where *i'* indexes the components for stage *j-1*. It is required that the components that flow from stage *j-1* to stage *j* appear in the both components lists. However, the indexing of a same component may vary from stage to stage. Hence, we use index *i'(i)* to signify the component index for stage *j-1* that corresponds to the component *i* of stage *j.*

As shown in Fig. 2(a), there can be two kinds of incoming streams to stage *j* for each component *i*; 1) process stream $F_{i'(i),j-1}$ continuing from stage *j-1* onto stage *j*, and 2) added stream $Q_{i,j}$ fed to stage *j* from outside. Similarly, there can be two kinds of outgoing streams for the same; 1) process stream $F_{i,j}$ leaving stage *j* and continuing onto stage *j+1*, and

2) waste stream $W_{i,j}$ leaving stage j for disposal (or processing into alternative products, which is not considered here).

Binary variable $y_{k,j}$ will be used to signify whether option k for stage j is selected (if the corresponding option is selected, $y_{k,j}$ equals to 1; otherwise $y_{k,j}$ equals to 0). These binary variables are the main decision variables of the ensuing optimization, which will determine the optimal pathway. In this work, we assume that only one option can be chosen for each stage. Therefore, we enforce the constraint

$$\sum_k y_{k,j} \leq 1 \tag{1}$$

Given this constraint, $F_{i,j}$ the flow of process stream leaving the stage j is given by:

$$F_{i,j} = \sum_k (y_{k,j} \cdot \hat{F}_{i,k,j}) \tag{2}$$

where $\hat{F}_{i,k,j}$ is the flow of component i in process stream leaving option k of stage j.

Table 2. Nomenclature

Indices	
i	component
i'	component (used to index those coming from the previous stage)
l	utility
j	processing stage
k	option/technological alternative
r	reaction
m	key reactant, a subset of i
Parameters	
$\alpha_{i,i',k,j}$	fraction of chemical i added with respect to the incoming flow of component i' in option k of processing stage j
$\beta_{l,i',k,j}$	fraction of utility l added with respect to the incoming flow of component i' in option k of processing stage j
$\gamma_{i,r,k,j}$	stoichiometric ratio coefficient of product component i during reaction r in option k of processing stage j
$\theta_{m,r,k,j}$	fractional conversion of reactant m during reaction r in option k of processing stage j
MW_i	molecular weight of component i
$\mu_{i,k,j}$	waste fraction of component i in option k of processing stage j
Binary variable	
$y_{k,j}$	binary variable; 1 if option k from stage j is selected and 0 if otherwise
Continuous variables	
$F_{i'(i),j-1}$	flow of component i in the process stream coming from stage j-1
$F_{i,j}$	flow of component i in the process stream leaving stage j
$Q_{i,j}$	flow of component i in the chemical/solvent stream added to stage j
$W_{i,j}$	flow of component i in the waste stream leaving stage j
$U_{l,j}$	flow of utility l added to stage j
$\hat{F}_{i,k,j}$	flow of component i in the process stream leaving option k of stage j
$\hat{Q}_{i,k,j}$	flow of component i in the chemical/solvent stream added to option k of stage j
$\hat{W}_{i,k,j}$	flow of component i in the waste stream leaving option k of stage j
$\hat{U}_{l,k,j}$	flow of utility l added to option k of stage j

Similarly, $W_{i,j}$, the flow of component i in waste stream leaving the stage j without continuing on to the next stage, is also represented by:

$$W_{i,j} = \sum_k (y_{k,j} \cdot \hat{W}_{i,k,j}) \tag{3}$$

where $\hat{W}_{i,k,j}$ is the flow of waste stream leaving option k of stage j. The same idea works for the inlet flows of $Q_{i,j}$ as well as $U_{l,j}$, which represents the utility stream added to stage j:

$$Q_{i,j} = \sum_k (y_{k,j} \cdot \hat{Q}_{i,k,j}) \tag{4}$$

$$U_{\ell,j} = \sum_k (y_{k,j} \cdot \hat{U}_{\ell,k,j}) \tag{5}$$

We assume that a sequence of tasks is occurring inside each option/technological alternative box, including (1) mixing (2) reaction and (3) waste separation. The mass balance of component i can be written by adding the consumption and generation terms due to the reactions with the help of parameters such as the stoichiometric coefficients and fractional conversions of key reactants. For example, let us take the case of 'transesterification'. As shown in Fig. 2(b), $F_{i'(i),j-1}$ represents the flow of the component i in the process stream (mainly containing the lipids) coming from the previous stage j-1. The addition of methanol and catalyst is each represented by $\hat{Q}_{i,j,k}$. The mass balance takes the general form of

$$\hat{F}_{i,k,j} = F_{i'(i),j-1} + \hat{Q}_{i,k,j} + \left(\sum_{r,m} (\gamma_{i,r,k,j} \cdot \theta_{m,r,k,j} \cdot \frac{F_{i'(m),j-1}}{MW_m}) \right) \cdot MW_i - \hat{W}_{i,k,j} \tag{6}$$

where $\hat{F}_{i,k,j}$ is the flow of process stream of component i leaving option k of stage j, $F_{i'(i),j-1}$ is the flow of process stream of component i (indexed as i' at stage j-1) going from stage j-1 to option k of stage j, $\gamma_{i,r,k,j}$ is the stoichiometric coefficient, and $\theta_{m,r,k,j}$ is the fractional conversion of reactants, $F_{i'(m),j-1}$ is the flow of reactant m coming from stage j-1, and MW_i is the molecular weight of components, and $\hat{Q}_{i,k,j}$ is the flow of externally added stream of component i, which is given by:

$$\hat{Q}_{i,k,j} = \sum_{i'} \left(\alpha_{i,i',k,j} \cdot F_{i',j-1} \right) \quad (7)$$

where $\alpha_{i,i',k,j}$ is the fraction of chemicals/solvents added.

$\hat{W}_{i,k,j}$ is the flow of waste stream leaving option k of stage j which is given by:

$$\hat{W}_{i,k,j} = \mu_{i,k,j} \cdot f_{i,k,j} \quad (8)$$

where $\mu_{i,k,j}$ is waste fraction and $f_{i,k,j}$ is given by:

$$f_{i,k,j} = F_{i'(i),j-1} + \hat{Q}_{i,k,j} + \left(\sum_{r,m} (\gamma_{i,r,k,j} \cdot \theta_{m,r,k,j} \cdot \frac{F_{i'(m),j-1}}{MW_m}) \right) \cdot MW_i \quad (9)$$

Flow of utility stream $\hat{U}_{l,k,j}$ fed to option k of stage j is given by:

$$\hat{U}_{\ell,k,j} = \sum_{i'} \left(\beta_{\ell,i',k,j} \cdot F_{i',j-1} \right) \quad (10)$$

where $\beta_{l,i',k,j}$ is the fraction of utilities added.

2.3.2 Objective Function

The objective function to be maximized was chosen as the yield of biodiesel, which is proportional to the flow of the biodiesel out of the final stage:

$$Yield \propto F_{biodiesel,7} \quad (11)$$

However, one can instead choose to maximize the overall profit, which is total sales – the operating cost, also consider the multi-objective optimization of maximizing the profit and minimizing the amount of waste streams.

2.4 Model Solution

The optimization model is formulated and solved in GAMS with the DICOPT solver (linked to MINOS) using database built in Excel. All problem data are entered and stored in Excel. GAMS reads the data from Excel, solves the optimization problem, and sends the results back to Excel.

The database developed contains the input values of the model parameters such as the stoichiometric coefficients and fractional conversions of the key reactants, fractions of the chemical/solvent added, fractions of the utilities added, fractions of the waste separations, and molecular weights of the components. The values of all these model parameters are taken from the published literature. These input values form the database are used to translate the generic form of the model equations to specific ones through the equations (1) – (10).

3. CASE STUDY

The proposed methodology is implemented to determine the optimal processing pathway for the production of biodiesel from microalgal biomass.

3.1 Biodiesel

Biodiesel is a renewable fuel for diesel engine. At present, it is derived from vegetable oil (e.g. soybean oil, canola oil, rapseed oil, sunflower oil, palm oil, etc.) and animal fat (Demirbas, 2011). However several concerns have been raised about the sustainability of biodiesel produced from vegetable oil and animal fats. An alternative feedstock of microalgae has received due attention in recent years. Microalgae is a non-food feedstock, and therefore gives several advantages over terrestrial food crops. Unlike other oil crops, microalgae grow extremely rapidly and many of its species are exceedingly rich in oil (Chisti 2007).

The superstructure is developed for the production of biodiesel from microalgal biomass as given in Fig. 1, and explained in section 2.2. The objective of the optimization formulation is to maximize the yield of biodiesel as given by equation (11). Mass balance constraints are described in section 2.3.1.

4. RESULTS AND DISCUSSION

The optimization results are investigated and discussed in this section. The basis for calculation of biodiesel yield is 25000 liters of wet microalgal biomass (concentration: 4 g/L, dried microalgal biomass: 100 kg). The recycling of chemicals/solvents is not considered here. The objective is to maximize the yield of biodiesel.

The optimization results are given in Table 3 and optimal flowsheet corresponding to the maximization of biodiesel is given in Fig. 3. The optimal flowsheet (Fig. 3) consists of the harvesting of microalgal biomass by flocculation using polyelectrolyte as a flocculent, drying of microalgal biomass, acidic in-situ transesterification of microalgal lipids, and post transesterification purification including methanol recovery by distillation, separation of biodiesel and glycerol layers, washing of biodiesel layer, and purification of the biodiesel.

The maximum biodiesel yield is found to be 29.040 kg/25000 liters of wet biomass. The amount of waste produced with this flowsheet is 25623.4 kg/25000 liters of wet biomass. The reason for the large waste production is the very low concentration of microalgal biomass, thus resulting in a large amount of water (24900 kg) in our raw material (microalgal biomass). Therefore the waste produced consists of a large amount of waste water which can be recycled and utilized for the growth of microalgae to reduce the waste.

The result of the optimization is shown in Fig. 3. From the harvesting stage, the first option has been selected; from the pre-treatment stage, again the first option has been selected; whereas from the lipid extraction stage, the empty box is selected, which implies that lipid extraction stage is bypassed; from the transesterification stage, the fifth option has been selected. Both the lipid extraction and transesterification tasks are carried out in one step, which is represented by option ‘5,5’, acidic in-situ transesterification. This is selected mainly due to its high conversion of microalgal lipids into biodiesel.

The Fig. 3 describes the production of biodiesel from microalgal biomass via in-situ transesterification.

We determined the optimal processing route that gives the maximum yield of biodiesel. Similarly the processing pathway that gives the maximum gross operating margin and/or the minimum waste can also be determined by using the same model.

Table 3. Optimization results

Yield of biodiesel (kg)	Waste (kg)	CPU time (s)	Iterations
29.040	25623.4	0.031	94

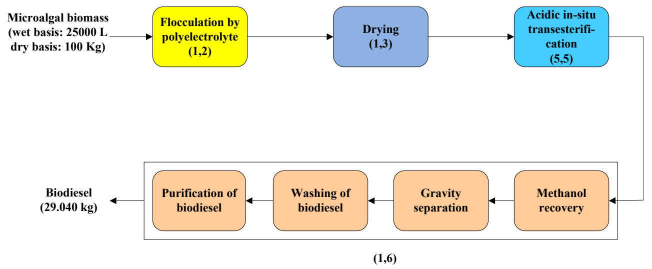

Fig. 3. Optimal flow sheet corresponding to maximization of biodiesel yield

The optimal processing pathway gives a large amount of waste mainly consists of water (which can be utilized for the growth of microalgae after recycling) and the microalgae residue which is left over after the extraction of lipid from microalgal biomass. This left over microalgal residue mainly consists of proteins and carbohydrate and can be processed further to produce valuable by-products such as biogas via anaerobic digestion. Similarly glycerol is the end by-product of biodiesel production which is produced during transesterification process. It can be separated and purified for further use. Finally the concept of microalgal biorefineries can be used to synthesize a processing pathway with less waste by conversion of biomass into useful industrial intermediates and final products by making essential and effective combinations of technologies.

5. CONCLUSIONS

In this paper, we have developed a mixed integer nonlinear programming (MINLP) model for the synthesis of biodiesel production process from microalgal biomass. The superstructure based optimization method has been presented in terms of problem definition, superstructure development, formulation of optimization model as MINLP and finally the solution. The objective of this study was to explore the implementation of this method to microalgal biorefineries area where we determined the optimal processing pathway for the production of biodiesel from microalgal biomass. The developed superstructure consisted of five processing stages (harvesting of microalgal biomass, pretreatment of harvested microalgal biomass, lipid extraction, transesterification, and post-transesterification purification). Corresponding to the objective function (the objection function was to maximize the yield of biodiesel), the optimal flowsheet was found. The proposed optimization model enables us to quickly scan many alternatives processing pathways.

This method is a systematic way for an optimal processing pathway and has the capacity to screen through all potential processing alternatives to locate the optimal processing network. Based on the obtained information, detailed process flowsheet can be synthesized for a more detailed economic evaluation. As future work, the modelling framework needs to be extended to accommodate choices of multiple products/pathways and further processing of waste streams into value products.

ACKNOWLEDGEMENT

This work was supported by the Advanced Biomass R&D Center (ABC) of Global Frontier Project funded by the Ministry of Education, Science and Technology (ABC- 2011-0031354).

REFERENCES

Chisti, Y. (2007). Biodiesel from microalgae. Biotechnology Advances, 25, 294–306.

Demirbas, A. (2011). Competitive liquid biofuels from biomass. Applied Energy, 88, 17–28.

Gouveia, L. (2011). *Microalgae as a feedstock for biofuels.* Springer Heidalberg Dordrecht London New York.

Grossmann, I. E. (1990). Mixed-integer nonlinear programming techniques for the synthesis of engineering systems. *Research in Engineering Design*, 1, 205–228.

Harun, R., Singh, M., Forde, G. M., Danquah, M. K. (2010). Bioprocess engineering of microalgae to produce a variety of consumer products. *Renewable and Sustainable Energy Reviews*, 14, 1037–1047.

Li, Y., Horsman, M., Wu, N., Lan, C. Q., Dubois-Carlero, N. (2008). Biofuels from microalgae. *Biotechnology Progress*, 24, 815–820.

Liu, P., Pistikopoulos, E. N., Li, Z. (2009). An energy systems engineering approach to polygeneration and hydrogen infrastructure systems analysis & design. *Chemical Engineering Transactions*, 18, 373–378.

Lynd, L. R., Wyman, C. E., Gerngross, T. U. (1999). Biocommodity engineering. *Biotechnology Progress*, 15, 777–793.

Quaglia, A., Sarup, B., Sin, G., Gani, R. (2012). Integrated business and engineering framework for synthesis and design of enterprise-wide processing networks. *Computers and Chemical Engineering*, 38, 213–223.

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, Jr W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R., Tschaplinksi, T. (2006). The path forward for biofuels and biomaterials. *Science,* 311, 484–489.

Yeomans, H., Grossmann, I. E. (1999). A systematic modeling framework of superstructure optimization in process synthesis. *Computers and Chemical Engineering*, 23, 709–731.

Zondervan, E., Nawaz, M., de Haan, A. B., Woodley, J. M., Gani, R. (2011). Optimal design of a multi-product biorefinery system. *Computers and Chemical Engineering*, 35, 1752–1766.