Energy Conversion and Management 156 (2018) 269–278

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Optimization of non-catalytic transesterification of microalgae oil to biodiesel under supercritical methanol condition

Garima Srivastava[a], Atanu Kumar Paul[b], Vaibhav V. Goud[a,b,*]

[a] Centre for Energy, Indian Institute of Technology Guwahati, Guwahati 781039, India
[b] Department of Chemical Engineering, Indian Institute of Technology, Guwahati, Guwahati 781039, India

ARTICLE INFO

Keywords:
Supercritical methanol (SCM)
Response surface methodology (RSM)
Artificial neural network (ANN)
Genetic algorithm (GA)
Chlorella CG12

ABSTRACT

The present study aims to maximize the conversion of microalgae oil to fatty acid methyl ester (FAME) using supercritical methanol (SCM) transesterification by sequential hybrid optimization using response surface methodology (RSM), artificial neural network (ANN) and genetic algorithm (GA). The three process parameters selected for the optimization of SCM transesterification were temperature (240 to 300 °C), time (15 to 45 min) and MeOH: oil molar ratio (15:1 to 45:1). Initial experiments performed according to the central composite design (CCD) generated matrix of RSM and further validated by ANN. The ^{1}H-NMR analysis confirms the formation of methyl esters. Moreover, the corresponding regression coefficient (R^2) for the model were 0.97 and 0.99 for RSM and ANN, respectively indicated excellent fit of the model to the experimental data. Furthermore, the final optimized condition for FAME conversion efficiency of RSM and ANN predicted models were 98.01% and 98.15%, respectively. The fitness function for GA was obtained from ANN predicted model equations and presented as globally optimized (GA conditions) reaction conditions for SCM: temp - 285.21 °C, time - 26.57 min and MeOH: oil molar ratio – 23.47. The predicted percent conversion efficiency of GA optimized conditions was 99.16% whereas, the experimental optimum FAME conversion reached to 98.12%. Additionally, the gas chromatography-mass spectroscopy (GCMS) analysis revealed the presence of palmitic (28%), oleic (33%), linoleic (8%) and other saturated and unsaturated fatty acids. The other biodiesel properties such as acid value, iodine value, cetane number, calorific value, etc. were also analyzed and exhibited an analogous trend with standard ASTM D6571 standards.

1. Introduction

Commercialization of algae biodiesel has been stymied due to the lack of process technologies. High processing cost and extensive energy requirement are the main hurdles for scale-up and development of an industrial level process for microalgae biodiesel [1]. Biodiesel is typically a mixture of fatty acid alkyl esters produced through transesterification reaction using strong acid or alkali as a catalyst. This conventional process has several drawbacks such as usage of catalyst, high energy consumption, production cost, complicated purification and separation process, the necessity to reduce free fatty acid content and release of hazardous chemicals to the environment [2]. Therefore, various optimization methods and technologies have been adopted for biodiesel production for improved recovery, intensification, and waste reduction by process system engineering [3,4].

Moreover, to overcome these limitations of the conventional transesterification process recently a catalyst-free method of supercritical methanol (SCM) transesterification was introduced by Japanese researcher Kusdiana and Saka [5]. The SCM process is an advanced, highly efficient, environment-friendly, less energy-intensive and superior technique for conversion of oil to fatty acid methyl ester (FAME) and is devoid of the use of catalysts. It reduces the experimental run time and processes high free fatty acid containing feedstock which was earlier not feasible to process by the conventional base-catalyzed process [6].

Fluids above its critical temperature and pressure conditions, under compressed state, behave as a supercritical fluid and act as a good solvent for many substances. The critical temperature and pressure conditions for methanol are 239 °C and 8.09 MPa. At this supercritical state, methanol behaves as a non-polar solvent and is capable of dissolving oil sample uniformly [5]. However, there are various reaction parameters that critically affect the efficiency of SCM transesterification process *viz.* reaction temperature, reaction pressure, residence time, MeOH: oil molar ratio and mixing intensity, illustrated in Table 1.

Recently the advantages of SCM over standard homogenous base catalyzed method have been systematically studied by Sawangkew

* Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology, Guwahati, Guwahati 781039, India.
E-mail address: vvgoud@iitg.ernet.in (V.V. Goud).

https://doi.org/10.1016/j.enconman.2017.10.093
Received 12 August 2017; Received in revised form 8 October 2017; Accepted 29 October 2017

Table 1
Effect of process parameters on SCM transesterification.

Oil sample	Temperature (°C)	Time (min)	MeOH:oil (molar ratio)	FAME Con[#] (%)	References
Jatropha oil	350	10	40.1	84.6	[7]
Canola oil	350	15	40:1	96.5	[8]
Soybean oil	325	60	43:1	84	[9]
Algae	265	20	9:1[*]	67	[10]
Rapeseed oil	350	15	42:1	93	[11]
Tobacco	300	90	43:1	92.8	[12]
WCO[**]	287	30	41:1	99.6	[13]
Palm oil	400	20	12:1	90	[14]
Microalgae oil	320	31	19:1	90.8	[15]
Microalgae oil	340	35	33:1	87.8	[15]

* Wt./vol. ratio.
** Waste cooking oil.
\# Conversion efficiency.

(2010) and it was proposed that extreme reaction conditions of high temperature (320–350 °C), pressure (19 to 45 MPa) and MeOH: oil molar ratio (40:1 to 42:1) should be maintained for high biodiesel yield and conversion [16]. However, another report suggests that extreme reaction conditions may lead to thermal degradation of fatty acid methyl esters (FAME) [17]. SCM transesterification performed at extreme temperatures between 325 °C and 420 °C with saturated (16:0 and 18:0) and unsaturated (18:1) fatty acids unveiled thermal decomposition of FAME due to isomerization, hydrogenation, and pyrolysis [17]. Therefore, several researchers have suggested high MeOH: oil molar ratio (MR) to reduce this extreme temperature [12,18,19]. Thus, in SCM transesterification process 42:1 MR of MeOH: oil is preferred to avoid the excessive rise in temperature. However, excess methanol is the major nuisance for the development of SCM process at industrial scale. Therefore, development of techno-economical and eco-friendly SCM process is essential for the sustainable production of biodiesel.

Simulation-based SCM process improvement provides better assumptions, skilled development of reaction conditions and removes non-adequate parameters that lead to speculative results. Marulanda (2012) has performed a simulation of SCM process for biodiesel production using Aspen Plus 2006 [20]. Shin et al. (2012) optimized biodiesel production from rapeseed oil by SCM transesterification, by implementing response surface methodology (RSM) [21]. Furthermore, Maran and Priya have selected RSM and ANN optimization for ultrasound-mediated intensification of biodiesel production from neem and muskmelon oil. They found that ANN had better approximation capabilities compared to RSM and yielded high transesterification efficiency [22,23].

Until the present, most of the biodiesel production optimization studies primarily conducted using RSM and ANN based approaches. Nevertheless, the problem with these two optimization methods (RSM & ANN) is their local approximation generalization. However, the individual experimental setup for local estimation is not feasible for the process system engineering due to the huge expense of energy and time. Therefore, genetic algorithm (GA), is one such technique to provide a global optimum condition. It is a prerequisite for developing optimization model to look after local optimization problems. GA is used for stochastic optimization with an aim to minimize the objective function based on "survival of the fittest" theory elucidated by Darwin [24]. GA creates solutions to the problem available in search space using its genetic operator, selection, crossing over and mutation [25]. Gradually, the less fit individual (experimental condition) die and new generations (conditions) evolved by recombination, crossing over and mutation. Hence, only the best-fit individual or optimized condition retain during selection over the several generations (iterations). Moreover, GA presents a global solution to the problem. In recent years, GA based on RSM and ANN models (as an objective function) have been applied successfully to optimize the input space of a bioprocess where RSM and ANN generated second-order polynomial equation was used as a fitness function [26,27]. Hence, computational intelligence techniques (artificial intelligence) can be used as tools for modeling, optimization, process intensification, supervision and control for biodiesel production centered on global optimization method and thus the processing system engineering become essential for establishing sustainable and less energy intensive method [3,28].

To the best of our knowledge, a global optimization method of SCM transesterification in microalgae oil has not been described previously. Thus, this report tries to give a clear insight on the systematic development of process optimization for improved conversion of microalgae oil to FAME *via* SCM transesterification.

2. Materials and methods

2.1. Biomass cultivation

The microalgae cultivation of *Chlorella* CG12 was performed under laboratory optimized conditions of light intensity 3460 lux, temperature 21.07 °C and pH 8.74 in a standard BG-11 medium. The details of optimized culture conditions have been extensively described in our earlier paper [29]. Photobioreactors for large-scale microalgae cultivation up to 100 liters were established in a batch mode for biomass accumulation. After the completion of cultivation period (20 days), the biomass was harvested by flocculation (using trivalent metal ion solution of $FeCl_3$), centrifuged (6000 rpm for 10 min), dried overnight at 60 °C and subsequently employed for lipid extraction.

2.2. Lipid extraction

The dried microalgae biomass was used for oil extraction by Bligh and Dyer method using chloroform:methanol:water ($CHCl_3$:MeOH:H_2O) solvent system [30]. The extracted oil was washed twice with 0.9% sodium chloride (NaCl) solution to remove debris and mixture was allowed to settle overnight for the phase separation. Lipid and other non-polar compounds were recovered in $CHCl_3$ phase, while pigments and polar molecules were separated into methanol and water phase. The excess solvent was evaporated under vacuum rotatory evaporator (Model No. R210, Buchi) and crude algal oil was used for transesterification.

2.3. Experimental procedure

The crude algal oil was used for non-catalytic SCM transesterification in a 200 ml autoclave batch reactor (Model No. 1734, Amar equipment, India). Algal oil and MeOH were premixed in a beaker at 60 °C for 5 min and poured into the reaction vessel at continuous stirring of 400 rpm (Fig. 1). The pressure inside the autoclave reactor was maintained by purging N_2 gas.

The experimental reaction conditions were designed using CCD matrix, based on preliminary experiments carried out in the laboratory. The major process parameters chosen for the study were; reaction temperature (°C), reaction time (min) and MeOH: oil molar ratio. In this work, the input variables and their levels were selected after careful investigation of each parameter. Supercritical methanol has mild critical conditions (T_c = 239 °C; P_c = 8.1 MPa). Moreover, in the literature, it is reported that temperature above 300 °C deteriorates the quality of fatty acid composition. Thus, the lower and upper boundaries for temperature range selected was between 240 and 300 °C. SCM reaction is a very fast process and usually get completed within 20–30 min (observed in the preliminary experiments). Therefore, the reaction time of minimum 15 min is considered as an adequate for the complete transesterification reaction under SCM condition, however to find out the most optimum time period reactions are carried out up to 60 min (data not shown). However, the higher reaction time of 60 min