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Research Article

Exergy Analysis of Ultrasonic-Assisted *ex-situ* Biodiesel Production from Spent Coffee Grounds

Cynthia Ofori-Boateng [1*], Marcos Lopez [2], Kit Bauer [3], Ethan Craft [4], Jillian Verbus [5], Tracy Yu [6]
[1, 2, 3, 4, 5, 6] *Biofuels Sustainability Research Group, Department of Chemical Engineering, University of Pittsburgh at Johnstown, Johnstown, Pennsylvania, USA*
[*] *Corresponding Author Email: cyo6@pitt.edu*

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ABSTRACT

Waste management has become a global menace due to increasing waste generation caused by high population growth as well as the lack of efficient management technologies. Spent coffee grounds (SCGs), which are the wastes generated from coffee brewing, are generated globally at an annual rate of about 6 million tons and contain significant amounts of oil (about 10 – 21 wt%) which can be harnessed for biodiesel production. Exergy analysis is a sustainability assessment tool which can pinpoint stages within a manufacturing process where the quality portion of resources (available to do work) is destroyed hence helping engineers to make informed decisions on sustainability. In this study, exergy analysis of ultrasonic-assisted ex-situ (where SCG oil extraction and transesterification are carried out separately) biodiesel production technology (including the ultrasonic SCG oil extraction, ultrasonic transesterification, SCG biodiesel purification steps) is carried out to determine its sustainability hence suggesting process improvement options. For 1000 kg SCG as wet feedstock with a total exergy content of 28,261 MJ processed in an ultrasonic-assisted transesterification unit, an overall process exergy efficiency of about 45.5% was recorded in generating biodiesel and glycerin. Both the ultrasonic extractor and reactor recorded the highest exergy efficiencies of about 72.99% and 86.92% respectively. It was found in this study that ultrasonic-assisted ex-situ transesterification of SCG significantly improved the exergy efficiency of the system due to improved product yield and significant reduction of reaction time. Thus, SCG represents a potentially sustainable source of biofuel in the long term using ultrasonic cavitation.

Keywords: Biodiesel, exergy analysis, ex-situ transesterification, sustainability, spent coffee grounds, ultrasonic transesterification.

INTRODUCTION

Due to the near exhaustion of fossil fuels, coupled with their environmental challenges, research and development (R&D) of renewable energies is being intensified especially in resource (energy and materials) expenditure for sustainable production and consumption. Considering the thermodynamic and environmental dimensions of sustainability, biofuels become more competitive to fossil fuels presently when the feedstock and raw materials utilized are obtained from eco-friendly sources which can concurrently address the challenges of waste management and resource expenditure in biofuels production [1].

Spent coffee grounds (SCGs), the most abundant waste products in the coffee industry, are generated at a rate of about 6 million tons per year worldwide [2] from about 10 million tons of coffee beans after the decaffeination process [3]. Often, SCGs are not reused and therefore end up as waste in landfills, which decompose over after some time and contribute to greenhouse gas (GHG) emissions which pose environmental concerns as they are disposed of in uncontrolled landfills. Moreover, SCG being highly acidic is found to lower the pH levels of soils hence rendering them unsuitable for sustainable agriculture. Dried SCG is found to contain about 10 – 21 wt% of oil with a higher heating value (HHV) of 30 – 41 MJ/kg depending on the coffee species as well as the extraction method [4, 5]. Despite this high potential of SCG as a ‘no-cost’ biodiesel feedstock, it is not utilized for commercial applications of biofuels.

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The growing request for clean energy coupled with the urge for sustainable technologies has accelerated extensive research into the transformation of waste into biofuels. One of the efficient and innovative means of converting SCG oil into biodiesel is by ultrasound assistance where acoustic waves in a form of ultrasonic cavitations are used to enhance the transesterification process at significantly shorter times. However, ultrasonic biodiesel production may be energy intensive which may result in high resource utilization hence lowering the overall exergy efficiency of the system.

Biodiesel is usually produced by transesterification reaction of triglycerides in oils with alcohols (mostly methanol) and facilitated using a catalyst to generate fatty acid esters (depending on the type of alcohol used) commonly called biodiesel as well as a by-product called glycerin. Ultrasonication generating cavitations can be applied to both the SCG oil extraction and transesterification reaction in an *ex-situ* process (where the oil extraction and transesterification processes are carried out in separate units) to enhance process efficiencies and products' yields and quality at significantly less time compared to the conventional method of producing biodiesel.

This study employed exergy analysis as a thermodynamic sustainability assessment tool to evaluate ultrasonic-assisted *ex-situ* biodiesel production process efficiency and destruction of resources in terms of exergy. Exergy is the quality part of energy available to do work, hence the most valuable form of energy. Exergy, unlike energy, according to the second law of thermodynamics, takes into consideration entropy generation resulting in resource destruction hence able to pinpoint inefficient locations within a production process where there could be process improvement for sustainable production. Exergy analysis combines the first and second laws of thermodynamics to assess the thermodynamic and environmental feasibilities of energy systems. Exergy and exergy analysis has been discussed extensively elsewhere [1, 6, 7]. In this study, thermodynamic sustainability indicators such as exergy destruction, exergy efficiency and environmental burdens in terms of exergy are examined and energy improvement options are suggested.

METHODOLOGY

2.1. Process Description and Aspen Simulation

The system boundaries for the ultrasonic-assisted *ex-situ* biodiesel production excludes the cultivation stages of coffee beans as well as the generation of SCG from the decaffeination process. The production of all other raw materials and energy resources such as sodium hydroxide, methanol, water, electricity etc. are outside the system boundary of this study. A functional unit of 1000 kg SCG was used as basis for the materials, energy and exergy calculations. **Fig. 1** summarizes the flow diagram generated by Aspen Hysys software after simulation.

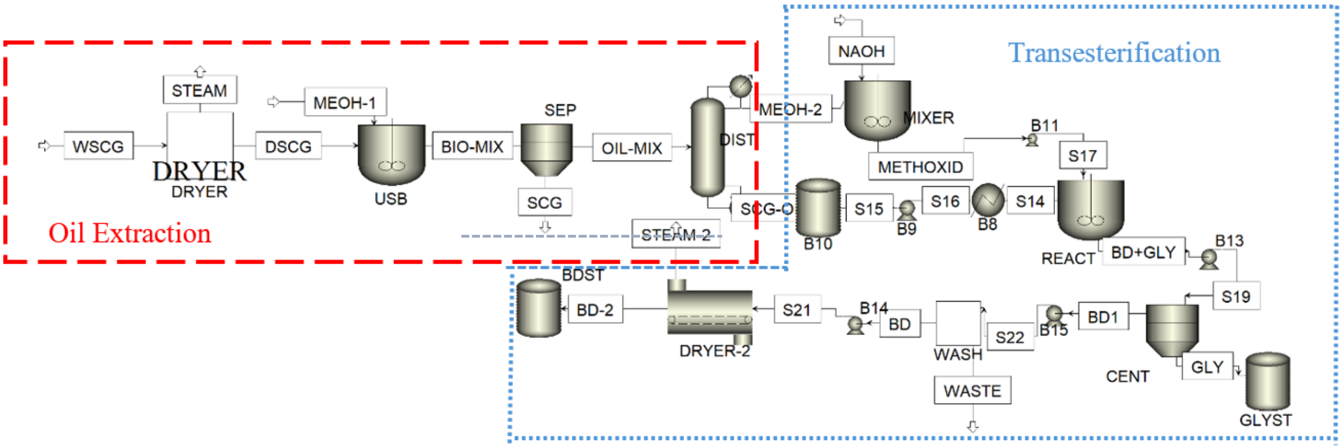

Figure 1. Aspen Hysys Flow Diagram of *ex-situ* Ultrasonic-assisted Biodiesel Production

As seen in Fig. 1, in the system boundary of ultrasonic-assisted SCG oil extraction, pretreatment of the wet SCG (WSCG) was carried out by drying in DRYER to reduce its moisture content to about 5 – 10 wt% (DSCG). Ultrasonic-assisted extraction was carried out in the reactor (USB) using methanol (MEOH-1) as solvent to obtain a mixture of oil, methanol and defatted SCG (BIO-MIX). This mixture is then separated in the SEP unit to obtain streams OIL-MIX (comprising methanol and SCG oil) and defatted SCG. Methanol is recovered (MEOH-2) by distillation in DIST whilst the SCG-oil is stored in B10 until transesterification. In the ultrasonic-assisted transesterification reactor (REACT), a mixture of NaOH (catalyst) and methanol (METHOXID) reacts with the SCG oil (S14) to form a mixture of biodiesel, glycerin methanol and traces of soap (BD-GLY). The glycerin layer (GLY) is separated in CENT and stored in GLYST whilst the biodiesel layer (BD1) comprising biodiesel, methanol and traces of soap is also washed with water in WASH to remove impurities. The biodiesel (S21) is then dried in DRYER-2 (to remove water and methanol) and stored in BDST until ready for use. The waste material (WASTE), which is mainly soapy water, is the major waste product in the biodiesel unit. The ultrasonic-assisted transesterification reaction was catalyzed and facilitated by eco-friendly chemicals like sodium hydroxide (NaOH) and methanol yielding about 99% biodiesel from the oil. The washer (WASH) operated at 80^{o}C, whilst the mixer (MIXER) and the centrifuges (SEP and CENT) were considered to operate at 25^{o}C and 1 atm.

Aspen Hysys software is a commonly used process simulator for modeling production processes. In this study, Aspen Hysys (v 10) was used to model the ultrasonic-assisted oil extraction and biodiesel production processes using the Peng-Robinson equation of state (PR-EOS) as the thermodynamic model. Biodiesel production stages involve complex mixtures of gases and liquids, mainly triglycerides, hydrocarbons etc. which may exhibit non-ideal behavior. Thus, the PR-EOS can accurately predict the activity coefficient and phase behavior of these complex mixtures hence enabling the ease of optimization and improvement.

The flows of materials and energy within the system boundary of the production processes were adopted based on laboratory and pilot scale ultrasonic-assisted biodiesel production data from literature [8, 9, 10]. Wet and dried SCGs as well as the extracted oil were assumed to comprise largely of the triglycerides, linoleic acid (C18:2), stearic acid (C18:0), palmitic acid (C16:0), and oleic acid (C18:1) [8]. Using methanol as a green solvent, an extraction time of 10 min and temperature of 55^{o}C, the ultrasonic-assisted oil extraction yield was assumed to be about 134.2 kg of SCG oil [8].

2.2. Exergy Calculation

The exergy of each stream was calculated, assuming a steady-state flow at standard conditions of 1 atm pressure and 25^{o}C temperature. Chemical exergy is the maximum amount of work obtainable when a substance is brought to a dead state from the environmental state by means of its chemical composition [6]. For instance, the chemical exergy of SCG oil was calculated based on the standard chemical exergies of its components (mainly triglyceride contents). For mixture streams, the chemical exergies were calculated based on the standard chemical exergies of the individual components in mixture using (1).

$$Ex_{ch,i} = \Delta G_{fo} + \sum_i v_i \, Ex^0_{ch,i} \qquad (1)$$

where $Ex_{ch,i}$, $\Delta G_{fo,}$ v_i, and $Ex^0_{ch,i}$ represents the chemical exergy of species i, the Gibbs free energy of formation, mole ratio of the ith component and standard chemical exergy of the ith component respectively. Using the standard chemical exergy of species in literature [11, 12, 13], the chemical exergies of the streams were calculated. The standard chemical exergies of biomass including SCG, SCG oil etc. were calculated in conjunction with data obtained from literature [6, 14].

Physical exergy of each stream was calculated based on the thermodynamic properties generated by Aspen Hysys software after simulation. At standard condition of T_0 = 298K and 1 atm, the physical exergy of each stream can be calculated from the enthalpy change ($H - H_0$) and entropy change (($S - S_0$) using (2).

$$Ex_{ph} = (H - H_0) - T_0 + (S - S_0) \qquad (2)$$

Exergy due to material resources is expressed by (3).

$$Ex_{mass} = Ex_{ch} + Ex_{ph} + Ex_{\Delta mix} \qquad (3)$$

where Ex_{ch}, Ex_{ph}, and $Ex_{\Delta mix}$ are chemical exergy, physical exergy and exergy of mixing of the system (assumed to be included in the physical exergy quantity) respectively.

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The overall exergy balance calculation based on mass transfer for a control region that connects the entropy generation to exergy destruction is expressed by (4) [15].

$$\sum Ex_{flow-in} - \sum Ex_{flow-out} = Ex_{destruction} = T_0 S_{generation} = I \quad (4)$$

where $Ex_{flow-in}$ = exergy of input resources

$Ex_{flow-in}$= exergy of output resources

$Ex_{destruction}$= exergy destruction

$S_{generation}$ = entropy generation

T_0 and I are the standard temperature (298 K) and irreversibility respectively.

Exergy destruction comprises internal exergy destruction ($Ex_{int\ dest}$) and exergy of waste into the environment ($Ex_{waste-to-env}$). Thermodynamic performance parameters like exergy efficiency and exergy destruction were used to determine the thermodynamic sustainability of the ultrasonic-assisted biodiesel production processes. Exergy efficiency is mathematically defined by (5).

$$Ex_{efficiency} = \frac{Ex_{flow-out}}{Ex_{flow-in}} = 1 - \frac{Ex_{destruction}}{Ex_{flow-in}} \quad (5)$$

where $Ex_{efficiency}$, $Ex_{destruction}$, $Ex_{flow-in}$ and $Ex_{flow-out}$ are the exergy efficiency, exergy destruction, exergy of input resources and exergy of output resources respectively.

For real-world processes, because exergy is not conserved unlike energy, the exergy input would exceed the exergy output often. This imbalance is because of entropy generation and irreversibilities leading to exergy destruction. In some situations where good quality materials which contribute to high chemical exergy content would be upgraded during the process and the input exergy would be less than the output exergy.

Exergy improvements potential can be expressed as a function of exergy destruction and exergy efficiency as defined by (6).

$$Ex_{imp-potent} = Ex_{int\ dest}\left(1 - Ex_{efficiency}\right) + Ex_{waste-to-env} \quad (6)$$

RESULTS AND DISCUSSION

Tables 1 and **2** show the chemical and physical exergies of input and output streams respectively. Aspen Hysys software generated enthalpy and entropy data which were used to calculate the physical exergies of the respective streams.

Table 1. Chemical Exergy of Some Inputs and Output Streams (1000 kg SCG)

Stream Name	Stream Number	Mass (kg)	Standard chemical exergy, $Ex^0_{ch,i}$ (MJ/kg)	Chemical Exergy $Ex_{ch,i}$ (MJ)
Ultrasonic Oil Extraction				
Wet SCG (Feedstock)	1	1000	28.261	28261.00
Dried SCG	3	894.7	20.00	17894.00
SCG cake (by-product)	6	760.5	21.83	16601.72
Recycled Methanol	5	4473.3	22.47	100,515.05
SCG oil (Product)	8	134.2	37.27	5001.63
Ultrasonic Transesterification and Biodiesel Purification				
SCG Oil (Feedstock)	8	134.2	37.27	5001.63

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Stream Name	Stream Number	Mass (kg)	Standard chemical exergy, $Ex^0_{ch,i}$ (MJ/kg)	Chemical Exergy $Ex_{ch,i}$ (MJ)
Sodium hydroxide (NaOH)	9	1.35	1.8725	2.53
Methanol (MeOH)	10	53.7	22.47	1206.64
Sodium Methoxide	11	55.01	26.09	2929.88
Transesterification reaction products	12	189.3	7.258	1373.94
Recycled methanol	13	50.6	22.47	1136.99
Glycerin (by-product)	16	5.8	22.30	129.34
Process water (liquid)	17	398.7	0.0499	19.90
Pure Biodiesel (product)	22	132.9	36.69	4876.10

Table 2. Thermodynamic Properties of Input and Output Streams (at 298K and 1 atm)

Stream / stream component	Mass (kg)	Enthalpy change ΔH (MJ/kg)	Entropy change ΔS (MJ/kgK)	Physical Exergy $Ex_{ph,i}$ (MJ/kg)	Physical Exergy $Ex_{ph,i}$ (MJ)
Dried SCG	894.7	-1.112	-0.00254	0.35508	317.69
SCG oil	134.2	-2.254	-0.0305	6.839	917.79
SCG Biodiesel	132.9	-1.9604	-0.0081	0.4534	60.26
SCG Glycerin	5.8	-0.4441	-0.0228	6.3503	36.83

Fig. 2 summarizes the exergy balance calculations for ultrasonic-assisted oil extraction units.

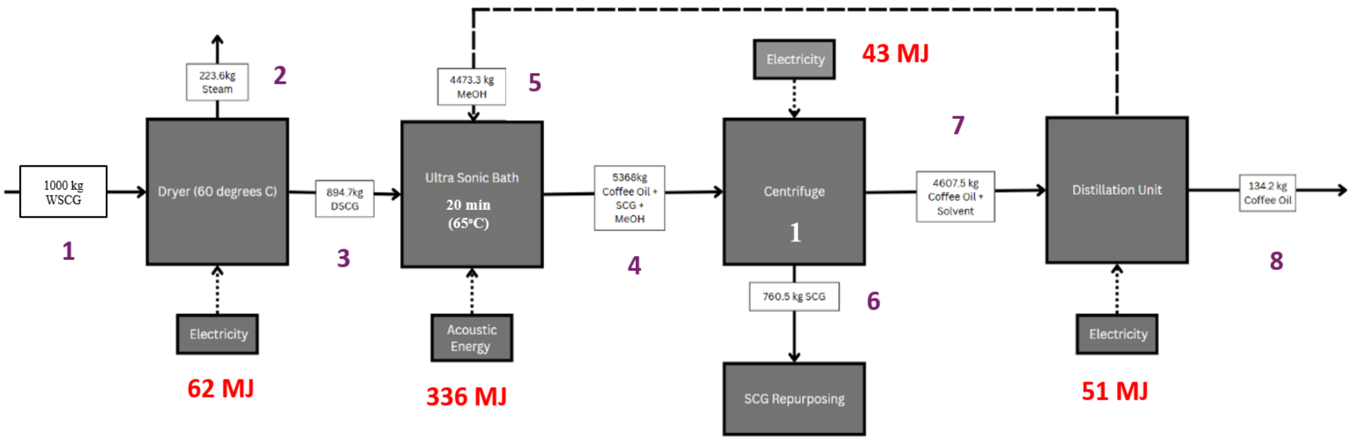

Figure 2. Ultrasonic-assisted Extraction of SCG oil Exergy Balance Flow Diagram

For 1000 kg of wet SCG (about 40 – 60 wt% moisture content) processed through ultrasonic-assisted oil extraction unit, a total of about 211,280 MJ of exergy was expended in the form of electricity, feedstock, utilities and raw materials to generate about 261,475 MJ total exergy of output materials comprising products (bio-oil) and by-products (exhaust steam and SCG cake/defatted SCG). This exergy upgrade of input materials to form the products is due to imbalance in the process units and low chemical exergies of raw materials (such as waste materials, eco-friendly resources etc.) that were used to generate high quality SCG oil, SCG cake and recovered methanol. This suggests a very high exergy efficiency above 100% for the oil extraction unit. However, when the by-products are further processed into useful products, the exergy efficiency could be reduced due to energy utilization, raw materials inputs etc. Thus, about 93% of the quality part of energy available to do work found in the input resources were converted to useful products when the SCG cake is assumed to be recycled, sold or transformed into value-added products. Gholami et al. [8] reported similar results (95.6% exergy efficiency) of ultrasonic assisted biodiesel production from canola oil. For *Jatropha curcas* and algae oil extraction without ultrasonic-assistance, about 61% and 62% of the products' exergy were useful respectively [13] which is lower compared to the results in this study.

In the oil extraction unit, the processing of 1000 kg of wet SCG into 134.2 kg oil resulted in an overall exergy destruction of about 314,861 MJ. This is higher compared to the report of Ofori-Boateng et al. [6] who concluded in their study that to produce about 928.7 kg of algal oil for biodiesel production via methanol extraction without ultrasonic-assistance, about 132,648 MJ of exergy was destroyed. Internal exergy destruction caused by entropy generation can result from turbulence which generates specific mechanisms of irreversibilities by means of flow through viscous materials, mass and heat transfer processes [6, 16].

The recycling of methanol from the distillation unit (see **Fig. 2**) back into the ultrasonic oil extraction unit would reduce the overall exergy destruction by about 42%. The main external exergy destruction, which is the exergy of waste products resulted from steam exhaust (128 MJ) from the dryer, which was vented into the atmosphere, and the SCG cake/defatted SCG after centrifugation (15,379 MJ). The centrifuge 1, which separated the SCG cake from the organic phase (mixture of biodiesel, methanol, SCG solids etc.) recorded the highest exergy efficiency of about 85.4% because of minimal entropy generation. If the SCG cake is recycled for steam or electricity production for use in the plant or sold for other purposes, it would reduce the exergy destruction by about 71.5% hence increasing the overall efficiency of the oil extraction unit.

The least recorded exergy efficiency (57.6%) occurred in the distillation unit which was used to separate the methanol from the oil-methanol mixture. This could increase drastically when the recovered methanol with an exergy content of 182,527 MJ is purified for reuse in the plant. However, the internal exergy destruction because of entropy generation was minimal. The exergy content of the oil extraction unit's products may contribute to high exergy efficiency of the distillation unit when the process is scaled up. Solvent extraction and mechanical oil extraction methods are found to have higher exergy efficiencies (79.35% and 95.93% respectively) compared to ultrasonic-assisted oil extraction as recorded in this study (72.99%) due to the quantity of fossil based energy utilized in the process as well as the exergy content of the feedstock. **Fig. 3** summarizes the exergy destruction of the main unit operations in the ultrasonic-assisted SCG oil extraction unit.

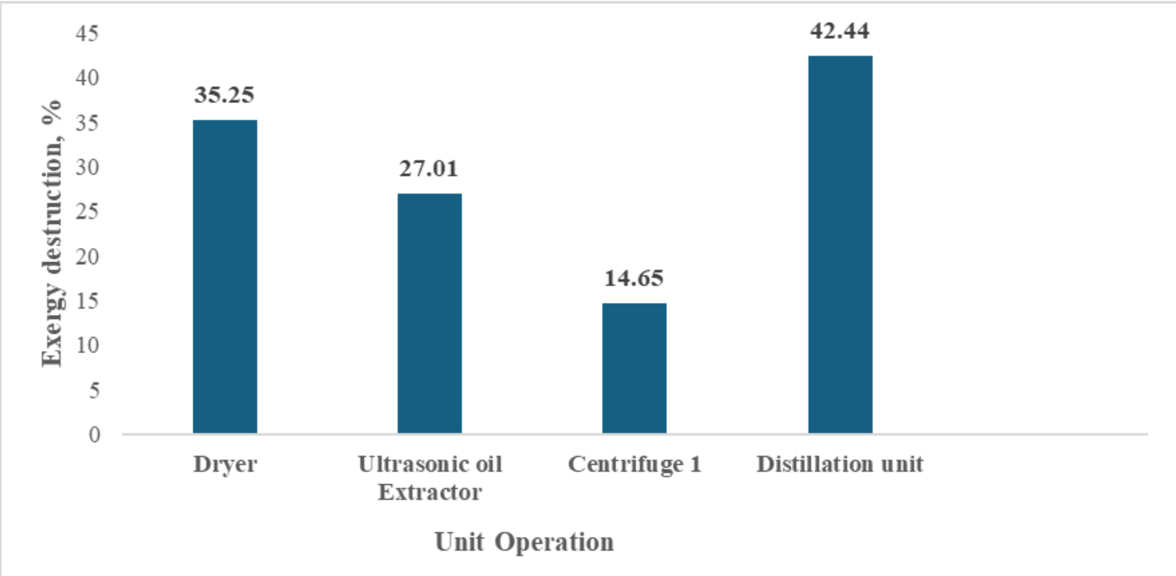

Figure 3. Exergy Destruction in the Unit Operations within the Ultrasonic-assisted SCG oil Extraction Unit

Fig. 4 summarizes the exergy balance calculations for ultrasonic-assisted transesterification of SCG oil into biodiesel. For a total exergy of 28,261 MJ of SCG feedstock processed, about 45.5% of exergy efficiency was recorded in producing the main products (biodiesel and glycerin).

In the biodiesel production unit, centrifuge 2, which separates the biodiesel and glycerin, recorded the highest exergy efficiency of about 94.9% due to less entropy generation and minimal irreversibilities in the unit. However, the biodiesel dryer recorded the lowest exergy efficiency (65.7%) due to entropy generation during heat transfer. **Fig. 5** shows the exergy efficiencies of the main units in the ultrasonic-assisted transesterification unit. In unit operations where heat transfer occurs like in dryers and distillation columns which record low exergy efficiencies, it becomes necessary to improve the equipment design and optimize the process.

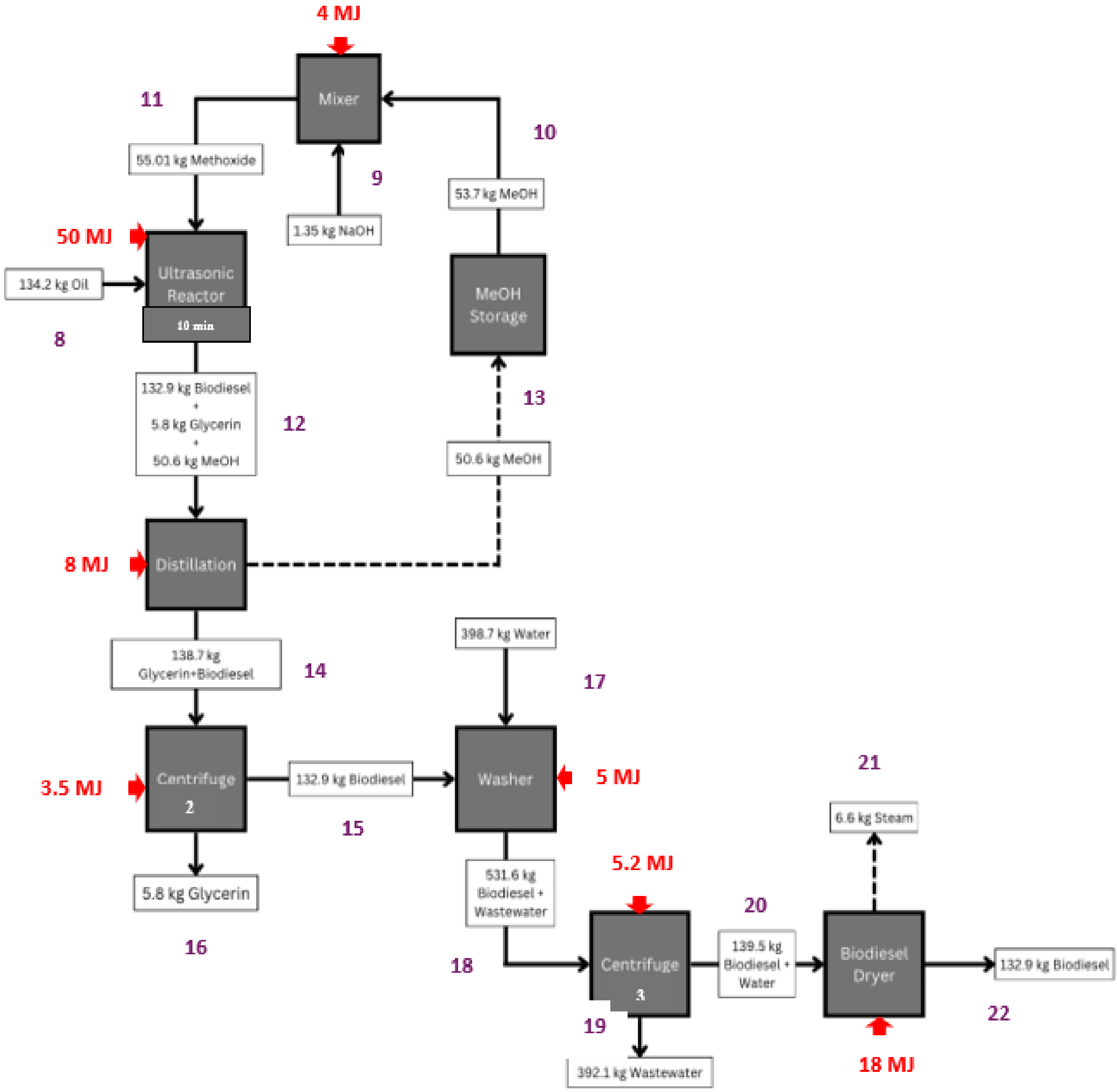

Figure 4. Ultrasonic-assisted Transesterification of SCG oil Exergy Balance Flow Diagram

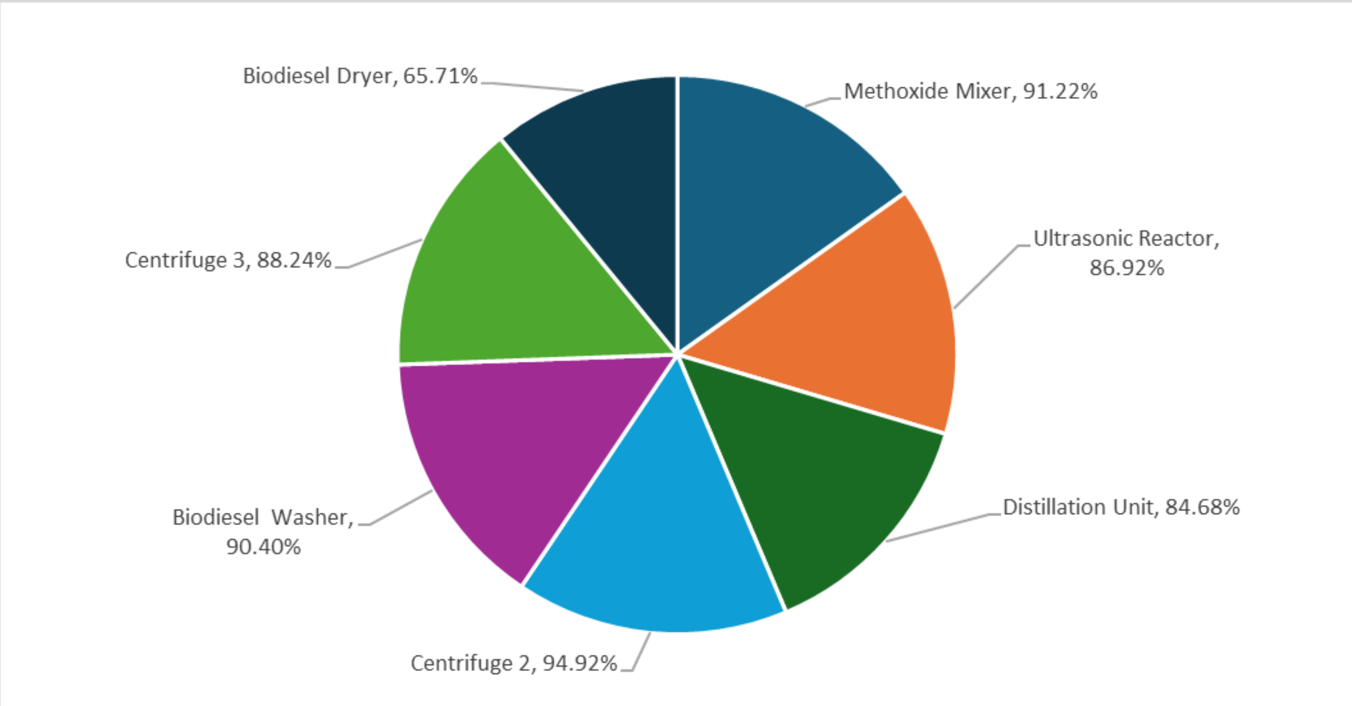

Figure 5. Exergy efficiencies in Unit Operations within the Ultrasonic-assisted Transesterification Unit

CONCLUSION

Exergy analysis is a sustainable assessment tool which can pinpoint stages within a manufacturing process where the quality portion of energy and materials or resources (available to do work) is destroyed hence helping engineers to make informed decisions on sustainability. In this study, exergy analysis of ultrasonic-assisted *ex-situ* biodiesel production technology was carried out for process improvement and sustainability. For a total exergy of 28,261 MJ of SCG feedstock processed, about 45.5% of exergy efficiency was recorded in producing the main products (biodiesel and glycerin). Both ultrasonic extractor and ultrasonic reactor recorded high exergy efficiencies of about 72.99% and 86.92% respectively. The total exergy destruction of about 49,177 MJ and 50,285 MJ were recorded for the oil extraction and biodiesel production units respectively, which are smaller compared to algae and jatropha biodiesel production units reported elsewhere. Overall, most of the units within the biodiesel plant recorded high exergy efficiencies. Thus, SCG represents a potential source of biofuel which can be sustainable in the long term when transformed into biodiesel by ultrasonic assisted means.

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