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Energy, Exergy, and Environmental Analysis and Optimization of Biodiesel Production from Rapeseed Using Ultrasonic Waves

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A B S T R A C T

Due to limited oil reserves, the rising world fuel prices and environmental problems caused by the use of fossil fuels increase the tendency to use alternative fuels such as biodiesel and bioethanol. In this study, the evaluation of energy and exergy flow from seed planting to final production of biodiesel from rapeseed oil was carried out. Biodiesel production from rapeseed was made in three main phases: farm, oil extraction, and industrial biodiesel production. Initially, the input and output variables for rapeseed production were collected through questionnaires from 30 rapeseed farms in Khuzestan province, Iran. Thus, the amount of energy input and output to the field for rapeseed was estimated to be 12826.98 and 22195 MJ/ha, respectively. The highest energy consumption is related to chemical fertilizers with 65 % share of other inputs. Input and output exergy rates were obtained as 3933.494 and 22603.39 MJ/ha, respectively, and the highest exergy consumption related to diesel fuel with 58 % share of other inputs. At the biodiesel production stage, the input energy and output energy were 156.95 MJ and 41.88 MJ, respectively, and the highest amount of electricity consumed was 91.02 MJ. The total amount of exergy in the production of biodiesel and the output exergy was 48.412 MJ and 64.568 MJ, respectively. In this study, the effects of alcohol-to-oil molar ratio, ultrasound power (W), catalyst concentration (w/w %), and the reaction time (min) on methyl ester yield using response surface methodology based on Box Behnken experimental design in the Design Expert software were investigated. Finally, gas emissions were studied at the planting and biodiesel production stages, and the resultsshowed that the highest greenhouse gas emissions at the planting stage were related to chemical fertilizers and alcohol production.

1. INTRODUCTION

World energy demand is steadily increasing due to economic growth and population. This growth is potentially problematic due to reduced non-renewable reserves, large-scale environmental degradation in the form of global warming, and atmospheric pollution caused by the combustion products of these fuels. To overcome the challenges of fossil fuels, renewable and alternative energy sources are now being searched for more than ever before. Biodiesel, derived from vegetable oils and animal fats, has been introduced as an environmentally friendly fuel as an alternative to diesel fuel [1, 2]. Until now, various sources have been introduced as biodiesel process feeds, which vary according to the materials and resources available in each region. One of these sources is oilseeds that is the second-largest food storage in the world. Rapeseed is one of the oilseeds whose cultivation has been considered as the main source of oil due to its adaptation to climate, resistance to drought stress, and alternation with cereals. FAO statistics show that rapeseed is the third-largest source of vegetable oil production in the world [3, 4]. This oilseed grows in most parts of Iran, and its oil content is about 40 to 45 % of the total grain weight [5]. Besides, rapeseed is currently the largest source of biodiesel production in the world. Biodiesel has been widely studied because of its attractive properties such as non-toxic, sulfur-free, oxygen content, biodegradable, and so on [6]. The triglyceride transesterification reaction is produced in the presence of a homogeneous/heterogeneous catalyst to intensify methanolysis [2, 7-9]. In order to produce biodiesel, ultrasound was used in this study. Ultrasonic irradiation has been shown to be one of the most promising techniques for converting different feedstocks to biodiesel by intensifying mass transfer of liquid–liquid heterogeneous medium [10]. The high energy contained in the ultrasonic irradiations generates cavities in the immiscible liquids, leading to the formation of micro fine bubbles. This in turn disrupts the phase boundary owing to the asymmetric collapse of generated microbubbles. Accordingly, a severe emulsification of the system close to the phase boundary is achieved due to the development of micro jets by violently impinged liquids [10].

A key indicator in producing a new energy source is its energy efficiency, which is the correlation between energy and exergy in the products received [11-13]. Energy use in agriculture is divided into direct and indirect energy consumptions [14]. Direct energy consumption in agriculture is achieved through the use of fuel and electricity [15], and indirect energy consumption in agriculture is provided by fertilizers and chemical materials [16]. The exergy method is a relatively new and alternative based on the energy concept, which is defined as a universal measure of the potential of work or the quality of various forms of energy in relation to a given environment. The exergy equilibrium applied to a process or an entire plant tells us how much of the potential

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work potential usable as the input to the system in question is consumed (irreversibly destroyed). The disappearance of exergy, or irreversibility, provides a fully functional measure of process inefficiency. Many studies have been done on the exergy investigation of biodiesel production including the study of Hou and Zheng (2009) who proposed a novel design using solar-powered steam and electricity to produce biodiesel [17]. In another study, Jaimes et al. (2010) conducted an exergy analysis of biodiesel production from palm oil [18]. A study of the production of biodiesel from Microalga and Jatropha was also conducted by Ofori-Boateng et al. (2012) [19]. In another study, the amount of ExROI (exergy return on investment) and the renewable factor for biodiesel from cooking oil was calculated, indicating better stability of this source than other vegetable oils [20].

One of the factors affecting human health and the environment is greenhouse gas emissions during the agricultural life cycle. Understanding and evaluating the product life cycle is one way of measuring greenhouse gas emissions. Greenhouse gas emissions and their effects on global warming are one of the major challenges for developed and developing countries. Under the Kyoto Protocol, countries are required to calculate and report their greenhouse gas emissions [21]. According to the National Geographic Magazine, more than a million species of plants and animals will be at risk by 2050 due to rising greenhouse gases and global warming. In addition to energy and exergy analysis as a way of energy management, determining the amount of carbon dioxide emitted per energy consumed can be used as an analytical tool to calculate pollutant levels along with energy and exergy analyses. Moreover, because agriculture has a large share of greenhouse gas emissions, environmental management is an important part of production systems to identify points of production that have the greatest environmental and greenhouse gas impact on the environment. Biofuels have become one of the main strategies in developed countries in recent years, and this is due to climate change as one of the major contributors to climate change, i.e., CO_2 emissions. CO_2 prevents heat from escaping into the atmosphere by creating a layer around the Earth, thereby causing global warming. In fact, CO_2 emissions are the main cause of global warming.

It should be noted that no studies have reported about investigating biodiesel production from rapeseed examine exergy side in Iran. In general, the purpose of the present study is to analyze the thermodynamic and environmental analysis of the process of rapeseed production in the field and the process of biodiesel production from its seed oil.

2. MATERIALS AND METHODS

2.1. Energy and exergy cycle analysis method

Biodiesel production from rapeseed was made in three main phases: farm, oil extraction, and industrial biodiesel production. Initially, the input and output variables for rapeseed production were collected through questionnaires from 30 rapeseed farms of Khuzestan province in Iran. Inputs used in the production of rapeseed include labor, diesel fuel, chemical fertilizers, chemical pesticides, and seeds; on the other hand, the output is the amount of rapeseed production. The second stage of rapeseed oil extraction and the final stage (biodiesel production) were conducted at the Bioenergy and Renewable Energy Research Center of Tarbiat Modares University.

2.2. Main principles of exergy and energy analysis

Four equilibrium Equations (1 to 4) for work and heat processes (mass, energy, exergy, and entropy) were used to analyze energy and exergy of cultivation and methyl ester production of rapeseed oil [22]:

Mass balance:

$$\sum m_{in}=\sum m_{out} \tag{1}$$

Energy balance:

$$\sum(mb)_{in}-\sum(mb)_{out}=W-Q \tag{2}$$

Exergy balance:

$$\sum(mb)_{in}-\sum(mb)_{out}+\sum\left(1-\frac{T_0}{T_K}\right)Q_K-W=l \tag{3}$$

Entropy balance:

$$S_{generation}=\sum(ms)_{out}-\sum m_{in}\sum-\frac{Q_K}{T_K} \tag{4}$$

where Qk is the amount of heat transferred across the border (kJ), W is the work (kJ), b is the flow availability of a stream (kJ/kmol), H is the enthalpy (kJ/kmol), m is mass (kg), T is temperature (°K), and S is entropy (kJ/kmol K).

Therefore, the first step of this analysis is to convert all inputs and outputs to their energy and exergy equivalents, given their equivalent coefficients according to Table 1.

Table 1. Energy and exergy input coefficients of different inputs and outputs on the farm.

Input/Output	Unit	Energy factor (MJ/unit)	Source	Standard chemical exergy Ex0 ($kJ \cdot kg^{-1}$)	Source
Inputs					
Nitrogen	kg	78.1	[5]	11,450	[23]
Phosphate	kg	17.5	[24]	3137	[23]
Potassium	kg	13.7	[5]	258	[23]
Herbicides	-	288	[24]	25,000	[23]
Electricity	kWh	11.21	[25]	-	[23]
Diesel fuel	L	47.8	[26]	47,840	[23]
Labor force	h	1.96	[27]	0	[23]
Rapeseed seed	kg	25	[28]	27470	[23]
Output					
Rapeseed	kg	25	[28]	25460	[23]

2.3. Rapeseed oil production

At the cultivated stage, raw seeds are found as the main crop and straw as the by-product. Raw seeds should be dried and stored prior to the extraction process, which can be either physical (pressing) or chemical (solvent extraction). In this study, extraction using hexane is considered as a solvent, obtaining crude oil as the main crop and rapeseed meal as a common product, which can be used for animal feed. Then, to achieve a high-quality product, crude oil must be purified and treated using physical and therapeutic methods.

2.4. Transesterification and optimization of rapeseed oil into fatty acid esterification (FAE)

2.4.1. Transesterification

At this stage of the experiment, the oil reacts in the presence of methoxide, resulting in the production of biodiesel and glycerin. The materials used in this study include methanol (Merck Co., Germany, 99.9 %.) and Potassium hydroxide (Merck Co., Germany, 99.8 %.). An ultrasonic processor (Topsonic Model, UP400, Iran) was used to perform the transesterification reaction (Figure 1). Finally, all inputs and outputs convert to their energy and exergy equivalents, given their equivalent coefficients according to Table 2.

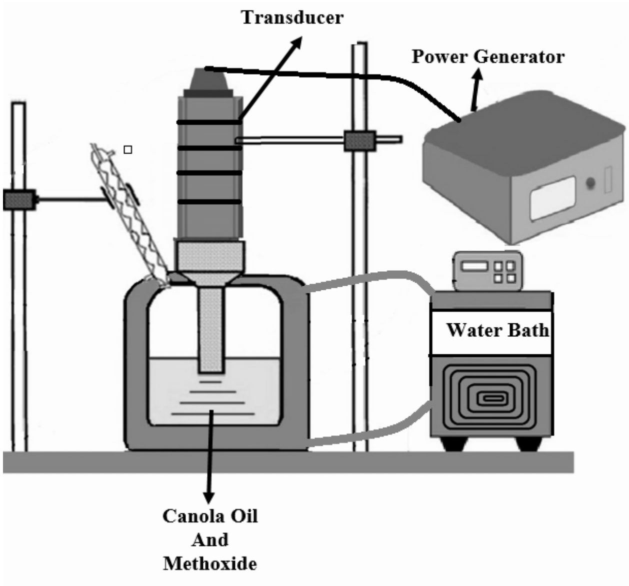


Figure 1. The schematic of setup biodiesel production.

Table 2. Energy and exergy coefficients in biodiesel production.

Input/Output	Unit	Energy factor (MJ/unit)	Source	Standard chemical exergy Ex0 ($kJ \cdot kg^{-1}$)	Source
Inputs					
Electricity	kWh	11.21	[25]	3.6	[23]
Rapeseed oil	kg	37.6	-	39930	[23]
Alcohol	kg	37.6	[29]	22360	[23]
Catalyst	kg	19.87	[30]	1867	[23]
Outputs					
Biodiesel	kg	37.2	[31]	39790	[23]
Glycerin	L	5.06	[30]	18670	[23]

2.4.2. Statistical analysis

The design of the present study is the response-box-Behnken method by the Design Expert software version 7. The response surface methodology is a set of mathematical and statistical techniques that are used to develop, promote, and optimize processes in which the level in question is affected by many variables, and the goal is to optimize the response. To derive optimal value, Regression Equation (5) is used [32, 33].

$$Y_i = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 + \varepsilon \qquad (5)$$

where βo, βi, βij, and βii are constant coefficients, xi and xj are independent variables in the process, and ε is random error. The levels of independent variables were selected according to Table 3.

Table 3. Independent variables on the experiment.

Independent variable	Coded level		
	-1	0	1
Molar ratio (Alcohol to Oil)	4:1	6:1	8:1
Power of ultrasonic (W)	160	280	400
Catalyst (w/w %)	0.75	1	1.25
Reaction time (min)	3	6	9

2.5. Environmental impacts

Environmental impacts of chemical fertilizers, diesel fuel, etc. were considered at the farm stage, and emissions from diesel fuel, electricity, natural gas, methanol, and catalysts were estimated in biodiesel production. Based on the number of inputs consumed and the CO_2 emission factor, the amount of greenhouse gas emissions was calculated according to Table 4.

Table 4. Greenhouse gas emission factor from inputs.

Inputs	Unit	Coefficient GHG (kg	Source
Machine	MJ	0.071	[25]
Diesel fuel	L	2.76	[25]
Chemical fertilizer	-	-	[34]
Nitrogen	kg	1.3	[34]
Phosphorus	kg	0.255	[34]
Potassium	kg	0.2	[34]
Electricity	kW h	0.78	[35]
Methanol	kg	0.79	[29]
Potassium hydroxide	kg	1.20	[29]

3. RESULTS AND DISCUSSION

3.1. Energy and exergy analysis at rapeseed cultivation

All farming activities were considered during the farming season to produce rapeseed. Table 5 shows the content of the inputs and output. To calculate the amount of energy and exergy, the amount of consumption or production of each data is multiplied by the energy and exergy coefficients (Table 1).

Table 5. Amount of energy consumption and exergy of inputs and output in agricultural production of rapeseed per hectare.

Input/Output	Consumption	The amount of energy consumption (MJ ha^{-1})	The amount of energy consumption (MJ ha^{-1})
Inputs			
Nitrogen	83.01	6483.081	950.4645
Phosphate	73.35	1283.625	230.099
Potassium	47.9	656.23	12.3582
Herbicides	6.36	1831.68	159
Electricity	-	-	-
Diesel fuel	48.1	2299.18	2301.104
Labor force	9.15	17.934	-
Rapeseed seed	10.21	255.25	280.4687
Output			
Rapeseed	887.8	22195	22603.39

Compared to the studies of rapeseed conducted by Mousavi-Avval et al. (2011), rapeseed has lower inputs consumption than other crops such as wheat in terms of inputs, manpower, fertilizer, fuel, machinery, etc. The reason for lower input consumption is the rainfed agriculture of rapeseed in the study region. Among the mentioned inputs, nitrogen was the most consumed due to vegetative need and, also, due to farmers' ignorance and excessive use of fertilizer (Table 5); therefore, the total input and the output energy were obtained as 2826. 98 and 22,195 MJ/ha, respectively. The amount of this energy varies from region to region because of the lower yield of the product in different regions, followed by less input energy being consumed. Energy consumption in chemical fertilizers with 65 % share is higher than other inputs. Among the chemical fertilizers, nitrogen was the most consumed with 50 % and flowing by diesel fuel with 17 % and herbicides with 14 %. Therefore, in order to reduce energy consumption, nitrogen fertilizer should be saved (Figure 2).

The total amounts of exergy input and output are 3933.494 and 22603.39 MJ, respectively. The highest amount of exergy consumption is related to diesel fuel with a 58 % share of all other inputs. Among chemical fertilizers, nitrogen with 24 % and rapeseed with 7 % had the highest exergy consumption among the inputs. Therefore, the largest share of exergy consumption is related to diesel fuel (Figure 3).

3.2. Investigation of biodiesel production performance

To determine the energy and exergy quantities in biodiesel production, it is necessary to calculate the amounts of the biodiesel and glycerol components, and the results are presented in (Table 1). The biodiesel production experiment was conducted to evaluate the yield of biodiesel production in 28 tests, and the results are reported in Table 6.

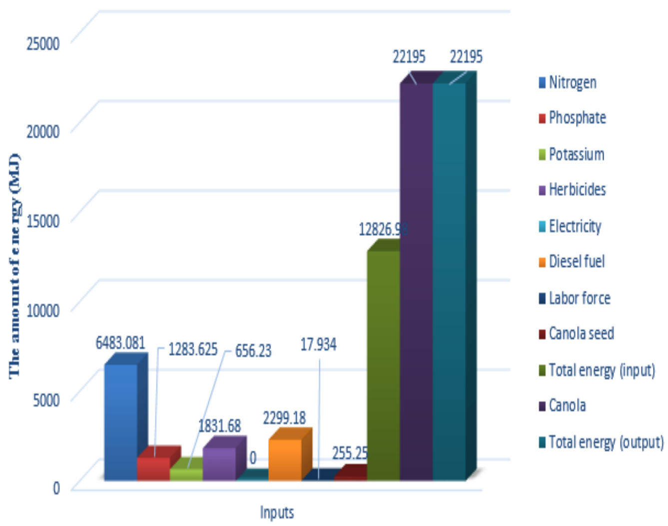


Figure 2. Input and output energy consumption of rapeseed production in the farms.

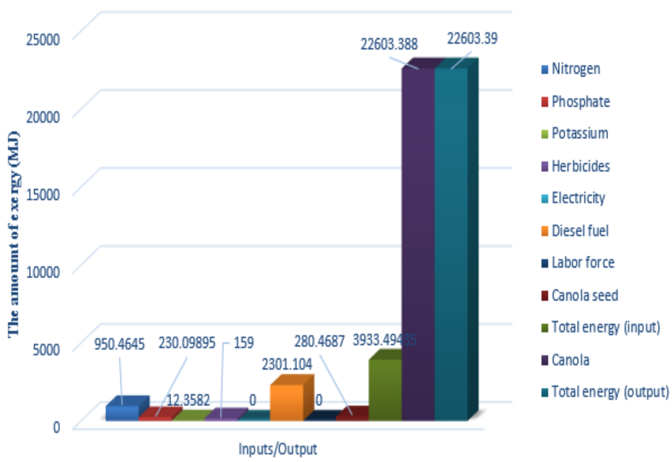


Figure 3. Input and output exergy consumption of rapeseed production in the farms.

Table 6. Full mass balance (kg) for the ultrasound-assisted biodiesel production from the rapeseed at different methanol/oil ratios, ultrasonic irradiation times.

Molar ratio	Time (min)	Catalyst (%)	Ultrasonic power (W)	Oil (kg)	KOH (kg)	Alcohol (kg)	Biodiesel (kg)	Glycerin (kg)	Yield (%)
4	6.00	1	400.00	0.05	0.0005	0.00687	0.032954	0.008231	76
8	9.00	1	280.00	0.05	0.0005	0.01358	0.044488	0.011112	93
4	6.00	1.25	280.00	0.05	0.000625	0.00687	0.030786	0.007689	71
8	6.00	1	400.00	0.05	0.0005	0.01358	0.042574	0.010634	89
8	6.00	1	160.00	0.05	0.0005	0.01358	0.040182	0.010037	84
6	6.00	1	280.00	0.05	0.0005	0.01018	0.039645	0.009902	87
6	6.00	1.25	400.00	0.05	0.000625	0.01018	0.038733	0.009674	85
4	3.00	1	280.00	0.05	0.0005	0.00687	0.030353	0.007581	70
6	6.00	1	280.00	0.05	0.0005	0.01018	0.0401	0.010016	88
4	6.00	1	160.00	0.05	0.0005	0.00687	0.032087	0.008014	74
4	9.00	1	280.00	0.05	0.0005	0.00687	0.034255	0.008555	79
6	3.00	1	400.00	0.05	0.0005	0.01018	0.037366	0.009333	82
6	6.00	0.75	160.00	0.05	0.000375	0.01018	0.037366	0.009333	82
8	3.00	1	280.00	0.05	0.0005	0.01358	0.037312	0.00932	78
6	9.00	1	160.00	0.05	0.0005	0.01018	0.041012	0.010243	90
6	6.00	0.75	400.00	0.05	0.000375	0.01018	0.038733	0.009674	85
6	6.00	1	280.00	0.05	0.0005	0.01018	0.0401	0.010016	88
6	3.00	1.25	280.00	0.05	0.000625	0.01018	0.033721	0.008422	74
6	9.00	1.25	280.00	0.05	0.000625	0.01018	0.039189	0.009788	86
6	9.00	1	400.00	0.05	0.0005	0.01018	0.042379	0.010585	93
6	6.00	1.25	160.00	0.05	0.000625	0.01018	0.035999	0.008991	79
6	6.00	1	280.00	0.05	0.0005	0.01018	0.039645	0.009902	87
8	6.00	1.25	280.00	0.05	0.000625	0.01358	0.038747	0.009678	81
8	6.00	0.75	280.00	0.05	0.000375	0.01358	0.040182	0.010037	84
6	3.00	0.75	280.00	0.05	0.000375	0.01018	0.035088	0.008764	77
6	9.00	0.75	280.00	0.05	0.000375	0.01018	0.0401	0.010016	88
6	3.00	1	160.00	0.05	0.0005	0.01018	0.035543	0.008878	78
4	6.00	0.75	280.00	0.05	0.000375	0.00687	0.030786	0.007689	71
6	6.00	1	280.00	0.05	0.0005	0.01018	0.039645	0.009902	87

3.3. Energy and exergy analysis at the biodiesel production stage

The F-value of Model is 547.41, indicating that the model is significant. In this case, A, B, C, D, AB, AC, BC, CD, B2, C2, D2 are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant.

Data analysis showed that the independent variables of molar ratio, ultrasonic power, catalyst concentration, and reaction time had a significant effect on the amount of methyl ester produced. The coefficient and standard error for the model are determined as 0.9982 and 8.433E-003, respectively.

$$\text{Energy} = -1.20194-2.49993E-004*A+2.40301*B+0.35710*C+0.032232*D+4.23787E-004*A*B+5.90778E-005*A*C-1.17719E-005*A*D-0.026693*B*C+5.65049E-003*B*D+5.07305E-003*C*D-3.30514E-007*A^2-1.22921*B^2-0.024698*C^2-2.65978E-003*D^2 \quad (6)$$

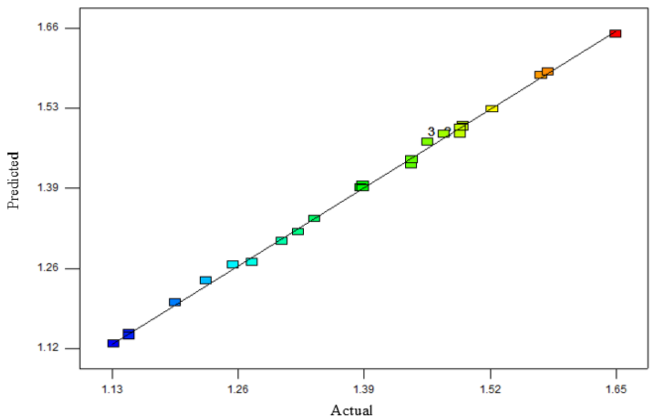
where A is the ultrasonic power (W), B is the catalyst concentration (w/w %), C is the molar ratio (Methanol alcohol to rapeseed oil), and D is time reaction (min). According to the coefficient of equation actual factor (6), the effective factors on energy consumption are molar ratio, time reaction, ultrasonic power, and catalyst concentration, respectively.

Table 7. Analysis of variance of the reactor performance.

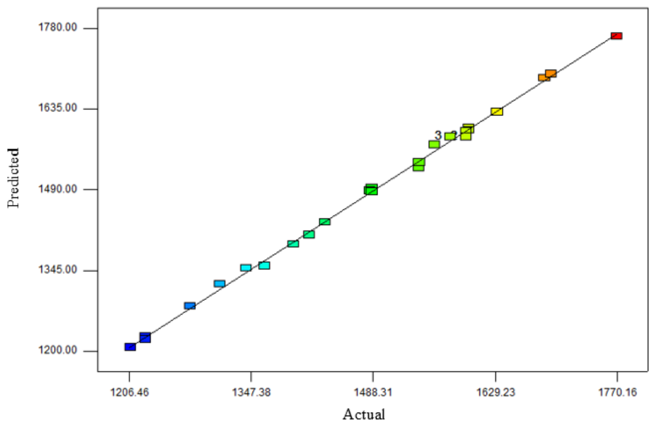
Source	Sum of squares	Df	Mean square	Significant factor
Model	0.54	14	0.039	< 0.0001
A-Ultrasonic power	0.013	1	0.013	< 0.0001
B-Catalyst Concenteration	2.977E-003	1	2.977E-003	< 0.0001
C-Molar ratio	0.32	1	0.32	< 0.0001
D-Time	0.12	1	0.12	< 0.0001
AB	6.465E-004	1	6.465E-004	0.0093
AC	8.041E-004	1	8.041E-004	0.0046
AD	7.184E-005	1	7.184E-005	0.3319
BC	7.125E-004	1	7.125E-004	0.0069
BD	7.184E-005	1	7.184E-005	0.3319
CD	3.706E-003	1	3.706E-003	< 0.0001
A2	1.469E-004	1	1.469E-004	0.1726
B2	0.038	1	0.038	< 0.0001
C2	0.063	1	0.063	< 0.0001
D2	3.717E-003	1	3.717E-003	< 0.0001
Residual	9.955E-004	14	7.111E-005	
Lack of fit	6.507E-004	10	6.507E-005	0.6741
Pure error	3.448E-004	4	8.621E-005	
Cor total	0.55	28		

Figures 4.a and 4.b illustrate the comparison of the actual data and the predicted data; given the shape and close compatibility of these numbers, there is a strong correlation between the results obtained by the experimental method and the values predicted by the statistical test.

Values of "Prob > F" less than 0.0500 indicate that the model terms are significant. In this case, A, B, C, D, AB, AC, BC, CD, B2, C2, D2 are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. The "Lack of Fit F-value" of 0.75 indicates that the Lack of Fit is not significant with respect to the pure error. The coefficient and standard error for the model are determined to be 0.9980 and 9.02, respectively.



(a)



(b)

Figure 4. (a) Actual data versus predicted data (enery), (b) Actual data versus predicted data (exery).

$$Exergy = -1285.62839- .26740*A+2570.31457*B+381.96073*C+34.47620*D+0.45329*A*B+0.063191*A*C-0.012591*A*D-28.55097*B*C+6.04390*B*D+5.42625*C*D-3.53525E-004*A^2-1314.78958*B^2-26.41758*C^2-2.84497*D^2 \quad (7)$$

According to the coefficient of equation (7) as the actual factor, the effective factors in total exergy include molar ratio, time reaction, ultrasonic power, and catalyst concentration, respectively.

Table 8. The results of the reactor performance model by the response surface method.

Source	Sum of squares	Df	Mean square	Significant factor
Model	6.235E+005	14	44534.91	< 0.0001
A-Ultrasonic power	14684.86	1	14684.86	< 0.0001
B-Catalyst concenteration	3405.57	1	3405.57	< 0.0001
C-Molar ratio	3.604E+005	1	3.604E+005	< 0.0001
D-Time	1.354E+005	1	1.354E+005	< 0.0001
AB	739.71	1	739.71	0.0093
AC	920.01	1	920.01	0.0046
AD	82.19	1	82.19	0.3319
BC	815.16	1	815.16	0.0069
BD	82.19	1	82.19	0.3319
CD	4239.97	1	4239.97	< 0.0001
A2	168.10	1	168.10	0.1726
B2	43800.80	1	43800.80	< 0.0001
C2	72429.52	1	72429.52	< 0.0001
D2	4252.54	1	4252.54	< 0.0001
Residual	1138.98	14	81.36	
Lack of fit	744.47	10	74.45	0.6741
Pure error	394.51	4	98.63	
Cor total	6.246E+005	28		

According to Figure (5a), with an increase in ultrasonic power from 160 W to 280 W, the biodiesel production energy increased to 0.05 MJ; in addition, by increasing the power to 400 W, the energy increased to 0.065 MJ. The highest energy consumption corresponds to the molar ratio of 1:4, ultrasonic power of 400 W, and reaction time of 6 min.

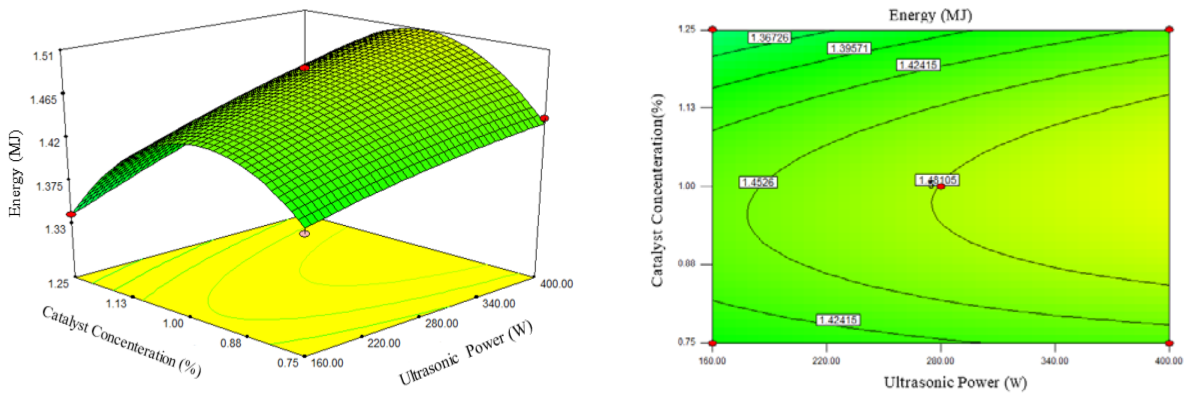
In fact, with an increase in ultrasonic power, the amount of electricity consumed increased; therefore, as the amount of consumed energy increased, the ultrasonic wave intensified the ration of chemical reactions by rising the mass transfer, generating intermediate phases between reaction phases, and increasing the intensity of reaction factors such as temperature and pressure [10].

Figure (6a) shows that with an increase in the ultrasonic power from 160 W to 280 W and, then, with an increase in 400 W, the biodiesel production exergy increased to 50.95 and 69.96 MJ, respectively. The highest exergy occurred at a molar ratio of 4:1, ultrasonic power of 400 W, and reaction time of 6 min. According to Fig. (5b, 6b), increasing the molar ratio from 4:1 to 6:1 increased the energy and exergy of biodiesel production to 0.27 and 289.85 MJ, respectively. In the next step, increasing the molar ratio to 8:1 increased energy and exergy to 0.32 and 346.6 MJ, respectively. The theory of this result is the balance of the transesterification reaction so that an increase in the amount of alcohol caused an increase in the methyl ester (biodiesel) production [36]. It is worth mentioning that an increase in alcohol is limited and dissolves glycerin and reduces the purity of biodiesel [37].

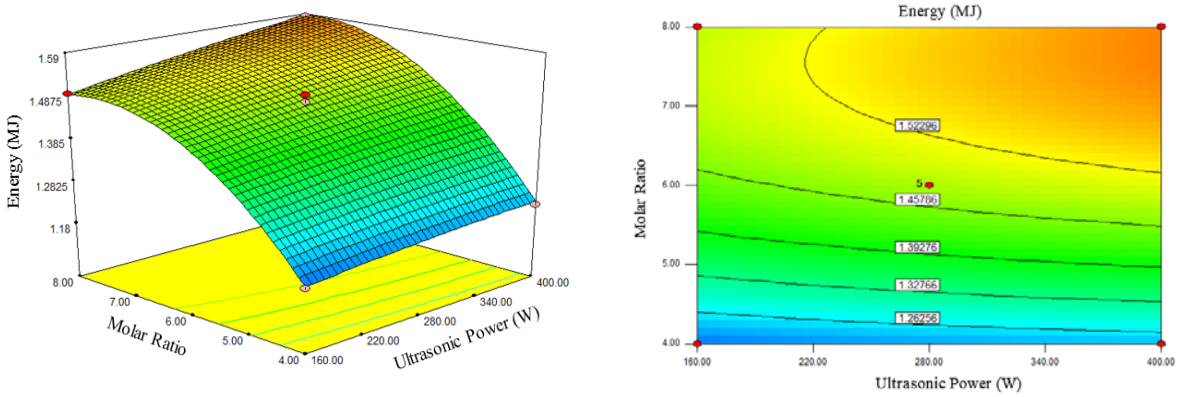
As shown in Figures (5c, 6c), increasing the catalyst concentration from 0.75 to 1 % increased the energy and exergy production of biodiesel to 0.071 and 76.21 MJ, respectively. In addition, when the catalyst concentration increased to 1.25 %, energy and exergy reduced to 0.3 and 33.69 MJ, respectively.

Reduced biodiesel production by increasing the KOH concentration is attributed to the soap formation [38].

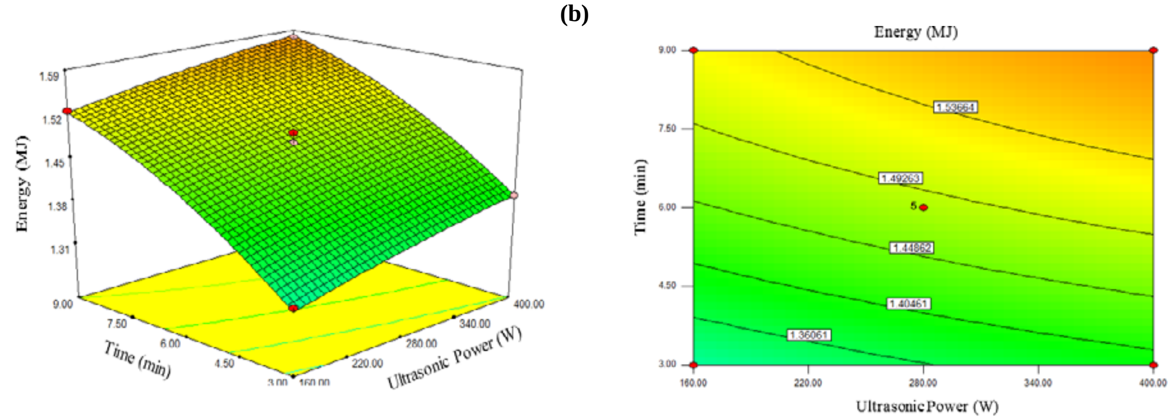
By increasing the reaction time from 3 to 6 minutes, the energy and exergy production of biodiesel increased to 0.13 and 142.72 MJ, respectively, and by increasing the reaction time to 9 min, the energy and exergy values increased to 0.19 and 212.47 MJ, respectively (Fig. (5c)).



(a)

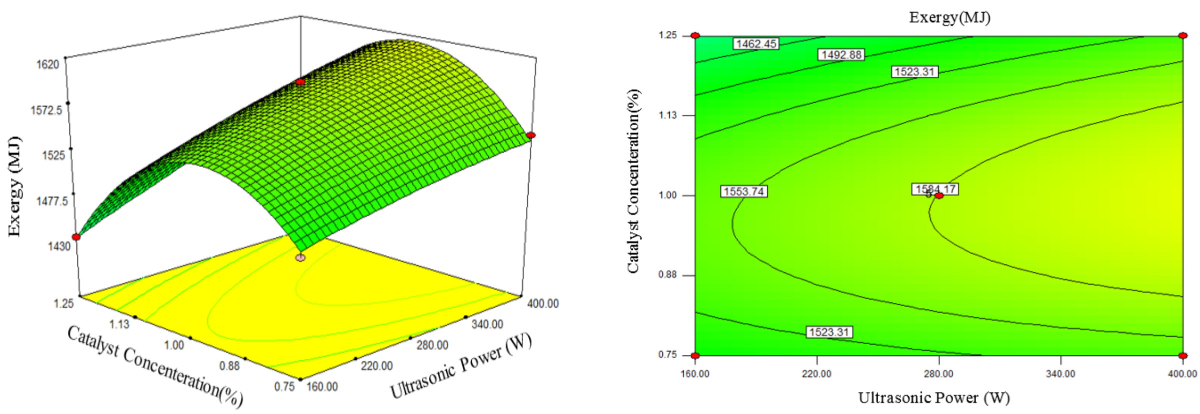


(b)

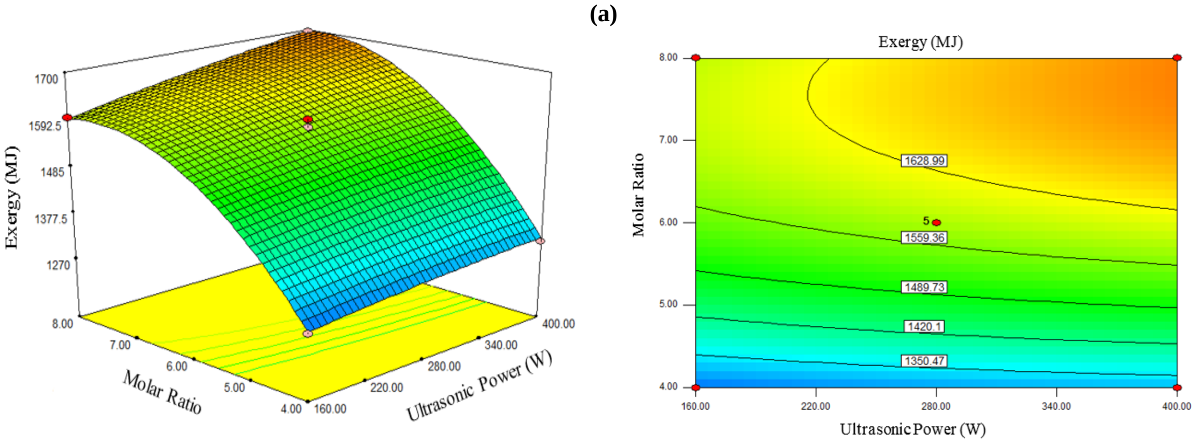


(c)

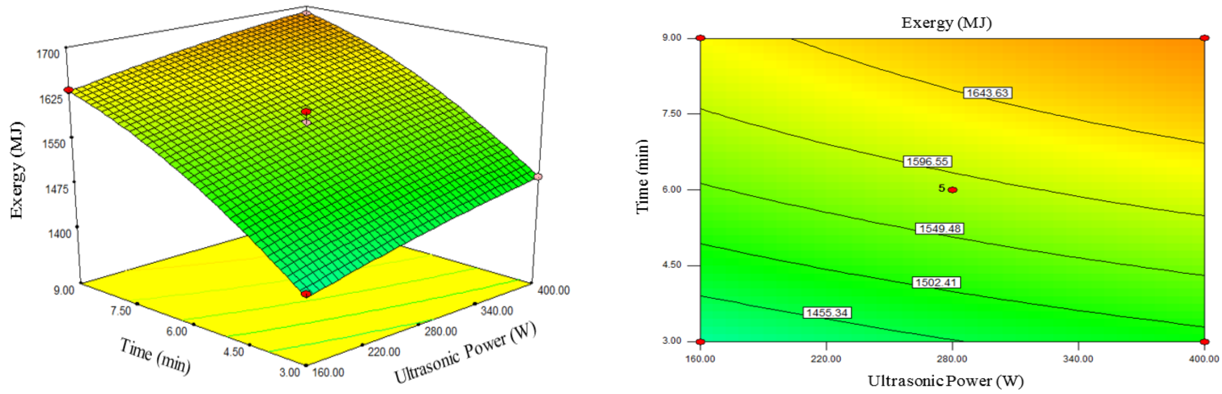
Figure 5. The interaction effects of (a) ultrasonic power (W)-catalyst concentration (w/w %), (b) ultrasonic power (W) molar ratio, (c) ultrasonic power (W)-time (min) on methyl ester conversion energy.



(a)



(b)



(c)

Figure 6. The interaction effects of (a) ultrasonic power (W)-catalyst concentration (w/w %), (b) ultrasonic power (W)- molar ratio, (c) ultrasonic power (W)-time (min) on methyl ester conversion exergy.

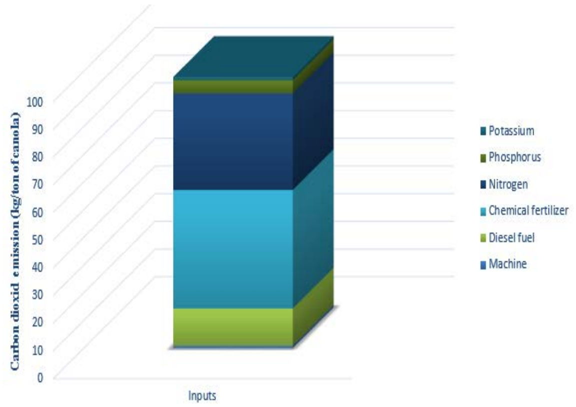
3.4. Greenhouse gas emissions analysis

The most effective factor in the potential of global warming at the agricultural stage is the high use of chemical pesticides with 41.1 % share and fertilizers, especially nitrate fertilizer with 33.5 % share. The results of the study showed that nitrogen dioxide and carbon dioxide emissions from chemical fertilizers and diesel fuel had the highest impact on the potential of global warming, respectively [39]. Studies have shown that agriculture plays an important role in the release of greenhouse gases into the atmosphere [34]. The main sources of emissions to the atmosphere include fossil fuels used in various agricultural operations, carbon losses from the soil due to tillage, burning of plant residues and forest trees, livestock, use of manures, and production and use of chemical fertilizers, especially nitrogen fertilizers [28]. According to Table (9), at the rapeseed seed stage, fertilizer consumption with 132.6 kg and 42.82 % shares had the highest impact on greenhouse gas production.Therefore, nitrogen fertilizer consumption (34.88 %) had the highest share of greenhouse gas emissions (Figure 7.a).

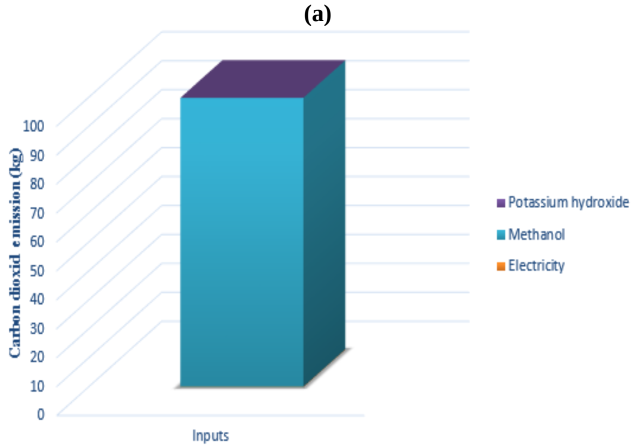
At the biodiesel production stage of rapeseed oil, methanol had the greatest impact on greenhouse gas emissions with a 99.81 % share (Figure 7.b). Biodiesel is an environmentally attractive fuel, because the results of its use have shown a significant reduction in greenhouse gas emissions compared to gasoline and diesel fuel. It also has lower methane emissions in its production cycle.

Table 9. Greenhouse gas emissions (kg CO_2 eq ha^{-1}) from rapeseed agriculture and biodiesel production.

Inputs	The amount of material	Percentage
Machine	2.7	0.87
Diesel fuel	41.6	13.43
Chemical	132.6	42.82
Nitrogen	108	34.88
Phosphorus	15	4.84
Potassium	9.7	3.13
Total	309.6	-
Electricity	0.08	0.15
Methanol	50	99.81
Potassium	0.012	0.02
Total	50.092	-



(a)



(b)

Figure 7. (a) Carbon dioxide emissions of rapeseed production, (b) Carbon dioxide emissions in rapeseed biodiesel production.

Grossman diagram (Figure 8) summarizes the results of exergy values of canola seed sowing stage, oiling stage, and biodiesel production from rapeseed oil. In order to calculate 1 tonne of rapeseed produced, the amount of oil obtained from rapeseed at the oil extraction stage was 295.9 kg; therefore, the exergy value of oil was 11815.287 MJ, and the exergy meal was 12026.53 MJ.

The rapeseed oil was the input of the biodiesel production stage; therefore, exergy was calculated in the optimum condition by Design-Expert software (molar ratio of 7, ultrasonic power of 160 watts, and oil catalyst concentration of 1 wt %). At each stage, the value and position of exergy loss are reported; therefore, the highest amount of exergy loss at the biodiesel production phase was 2845.71 MJ.

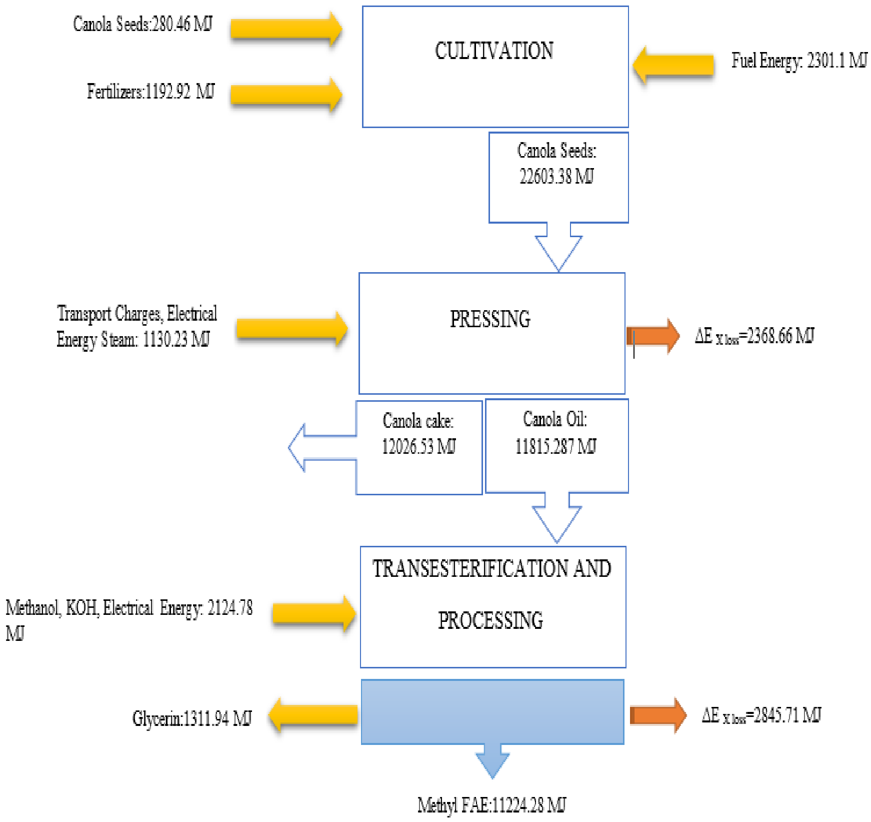


Figure 8. Grassmann diagram for methyl FAE production from rapeseed.

4. CONCLUSIONS

Energy and exergy of rapeseed crop cultivation and biodiesel production was evaluated using an ultrasonic reactor under laboratory conditions with variables of ultrasonic power, methanol to oil molar ratio, catalyst concentration, and reaction time. The results of the exergy index can be used to decide on the efficiency and sustainability of the biodiesel production system. In this study, the input and output energy of the field for cultivating rapeseed were 12826.98 and 22195 MJ/ha, respectively. The highest energy consumption was related to nitrogen fertilizer; therefore, energy consumption should be saved in order to reduce energy consumption. Input and output exergy rates were calculated and estimated to be 3933.494 and 22603.39 MJ/ha, respectively, and the highest share of exergy consumption was related to diesel fuel. In biodiesel production, the total energy input and output were 156.95 MJ and 41.88 MJ, and the highest exergy was associated with alcohol consumption.

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