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ORIGINAL PAPER

Environmental and energy analysis of biodiesel production in Rio Grande do Sul, Brazil

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Abstract Brazil's mandatory blending of 5.0 % biodiesel with diesel calls for an assessment of the environmental impacts of the biodiesel production process chain. Life-cycle Assessment (LCA) and energy efficiency analysis methodologies were used to assess biodiesel production from soybeans in Rio Grande do Sul state, Brazil. The study used a "Cradle to Gate" boundary and two levels in the energy analysis. The main results of the LCA were given in terms of environmental impact categories and indicated that phosphorus-rich fertilizers along with herbicides were responsible for major environmental impacts in the agricultural sector, whereas diesel accounted for greater damage in the soybean oil extraction sector. The influence of material flows in the refining of soybean oil varied according to the impact. The highest impacts were obtained using firewood to generate steam and phosphoric acid using sodium hydroxide for oil neutralization. Sodium methoxide and methanol more significantly influenced the transesterification step. Diesel affects all of the industrial sectors, mainly in relation to respiratory organics, the ozone layer, and fossil fuels, contributing no less than 50 % of the impact. Comparing the individual process sectors, the agricultural sector had the highest environmental impact. In terms of energy gain, biodiesel production presented a net energy gain of 3.08 units of useful energy when glycerin and soy meal are considered. Without these co-products, the process was very close to be unfavorable (1.04).

Keywords Renewable energy · Biodiesel · Life-cycle assessment · Energy efficiency

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Introduction

Currently, worldwide dependency on fossil fuels is unavoidable. Promoting greater use of renewable energy in the global energy mix is, therefore, necessary if greater sustainability is to be achieved. The Brazilian energy mix has a large share of renewable energy, reaching 42.4 % of total energy in 2012, a value significantly higher than the world average of approximately 13.2 % (MME 2013). Of all the renewables in Brazil, biomass has been highlighted as a promising option for the production of biofuels such as biodiesel. Increased production of these fuels has been targeted by large government incentives in recent years, for example, the 2004 creation of the National Program for Production and Use of Biodiesel (PNPB). Under the PNPB, the Brazilian government fixed a mandatory blend of 5.0 % biodiesel with fossil diesel (Stattman et al. 2013).

The existing production process and edaphoclimatic factors contribute to making biodiesel a viable alternative energy source in the Brazilian energy mix. The Southeast and South regions of Brazil, specifically the state of Rio Grande do Sul (RS), the southernmost state of Brazil, have major potential for biodiesel production (Bergmann et al. 2013). Today, RS has seven biodiesel plants, with a total biodiesel output capacity of approximately 5,000 m^3 day^{-1}, approximately 25 % of the total Brazilian production (ANP 2014; Padula et al. 2012).

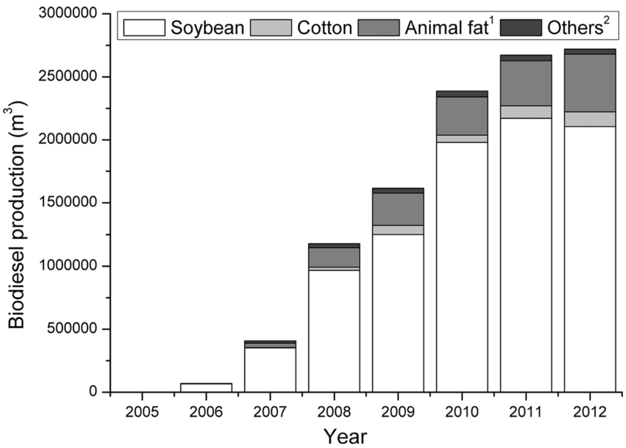

Fig. 1 Production of biodiesel from different feedstocks in Brazil, from 2005 to 2012. [1]Includes tallow, chicken, and swine fat; [2]Includes palm oil, peanut oil, sunflower oil, castor oil, cooking oil, and other fatty materials. *Source* ANP (2014)

Soybean is the most used feedstock, accounting for approximately 80 % of the total biodiesel production in the last three years in Brazil (ANP 2014), as shown in Fig. 1. Factors such as the tradition of soybean cultivation on large properties, regional climates, and appropriate agricultural technologies have resulted in a large abundance of soybean oil. Soybean oil is a byproduct of the soybean meal process, and the abundance of soybean oil has caused an oil surplus on the market, forcing down soybean oil prices.

Although biodiesel is an environmentally friendly fuel and biodiesel production pollutes less than conventional diesel (Özener et al. 2012; Qi et al. 2009), this resource is not free from environmental impacts. Many studies have focused their analysis only on biodiesel combustion in engines, ignoring the fuel supply chain. Additionally, the biodiesel production process may have a null or a negative energy balance, depending on the process, feedstock, and byproducts used (Hill et al. 2006; Nogueira 2011; Pimentel and Patzek 2005).

Life-cycle assessment (LCA) and energy efficiency analysis (EEA) are important tools that assist the environmental analysis of biodiesel production. Chouinard-Dussault et al. (2010) report that the integration of tools using mass and energy criteria is important to reduce mass and energy in the process. Although LCA and EEA are important, it should be emphasized that the results from these assessments must not be generalized to other situations (e.g., soybean biodiesel in Brazil). According to Milazzo et al. (2013), there are diversified soil conditions (wet/dry and rich/poor) and agrarian social structures (small/big farms) in Brazilian soybean cultivation, requiring LCA and EEA studies specific to each situation.

Soybean cultivation in RS is quite different from other states (mainly Central region states). In Brazil, the percentage of small family farms in soybean production was 16.0 %; in RS, this share is 33.0 % (IBGE 2006).

Thus, the aim of this work is to evaluate biodiesel production in RS from environmental and energy viewpoints, based on the identification, qualification, and quantification of process inputs and outputs. The results of such an effort can assist in improving processes adding value to products.

The applicability of the LCA and EEA methodology to biofuel studies is promising, and these methodologies are currently utilized in large-scale production with reasonable software limitations. In this sense, LCA of biodiesel production with SimaPro® and EEA become useful methodologies, in particular for RS.

Production of biodiesel

Harding et al. (2008) compared biodiesel production using inorganic catalysts in the presence of sodium hydroxide and biologics (enzymatic catalysis) to perform the transesterification reaction. Additional work by Morais et al. (2010) simulated the production of biodiesel, in environmental terms, via the conventional route with alkaline and acidic catalysts with supercritical methanol and propane as a co-solvent. Helwani et al. (2009) evaluated the production of biodiesel using homogeneous and heterogeneous catalysts in continuous and batch processes, emphasizing that continuous production is responsible for higher production capacity and lower production cost. Zhang (2003) compared the production of biodiesel in a continuous process using vegetable oil and waste cooking oil for both the alkaline and acidic routes. These results were given in terms of the number of equipment units required, and the study concluded that the alkaline route utilizing vegetable oil reduces the number of equipment units required but has a higher raw material cost. The use of waste cooking oil reduced raw material costs, but this process raised the equipment unit requirement. In a production process using only waste cooking oil, the acidic route was suggested instead of the alkaline process. Zhang et al. (2003), Marchetti et al. (2008) and Varanda et al. (2011) have studied the economic feasibility of biodiesel production.

Various conditions can result in operational problems and lower biodiesel conversion yield depending on the technological route being used. Specifically, the presence of free fatty acids and moisture in the oil illustrates the importance of dry and fatty acid-free (<0.5 %) oil (Freedman et al. 1984; Ma and Hanna 1999). Leung et al. (2010) note that alkaline transesterification is the route most used in the production of biodiesel and highlights the importance of the raw material purity. Specifically, the presence of water and humidity leads to hydrolysis, while free fatty acids lead to saponification, resulting in operational problems and reduced conversion. Other factors that affect biodiesel yield are also addressed (amount of alcohol, reaction time, reaction temperature, and catalyst concentration).

Meher et al. (2006) reported that the stoichiometry of transesterification requires three moles of alcohol per mole of triglyceride (3:1) yielding three moles of fatty acid ester (biodiesel) and one mole of glycerin. In practice, excess alcohol is used to shift the reaction equilibrium toward product formation, with an average molar ratio of 6:1 (six moles of methyl alcohol to one mole of triglyceride) used in most of the research on the alkaline route, as reported by Freedman et al. (1986).

According to Jardine et al. (2009), alkaline catalysts are most commonly used by Brazilian industries because these catalysts require lower operating temperatures and accelerate the reaction approximately 4,000-fold more than acidic catalysts; furthermore, alkaline catalysts require a lower molar ratio of alcohol to fatty acid. The major drawback of alkaline catalysis is their high sensitivity to reactant purity with respect to the water and free fatty acids present in vegetable oil and animal fat. Additionally, reaction temperatures must be lower than the boiling point of the alcohol used for esterification to ensure that the alcohol does not vaporize, preventing the loss of alcohol and improving the conversion of reactants into biodiesel.

According to Rinaldi et al. (2007), the transesterification of triglycerides occurs in three stages. In the first two stages of the process, triglycerides are rapidly transformed into diglycerides and monoglycerides. However, the conversion of monoglycerides into biodiesel is the slow step of the process, and the duration of the first two stages must be controlled.

In RS, biodiesel from soybeans is exclusively produced via a process that uses methanol and sodium methoxide (catalyst) for alkaline transesterification (Brondani and Hoffmann 2012); therefore, this route to biodiesel is assessed in this study.

Life-cycle assessment (LCA)

According to Ferrão (1998), "life-cycle" refers to all of the steps and processes related to production and consumption of a production system or service, including energy intake, raw materials, and auxiliary products, aspects of the transport systems and logistics, handling, packaging, marketing, and consumption, and lastly, waste production and recycling or other final destinations. The information collected in the LCA and the results and interpretations of the analysis can be useful for selecting environmental indicators that can be used to assess project performance as well as aid in project redesign and/or strategic planning (Chehebe 1998).

The International Organization for Standardization (ISO) is responsible for the standardization of the LCA methodology, numbered according to series: ISO 14040 (Basic Principles and Structure), ISO 14041 (Purpose, Scope and Inventory Analysis), ISO 14042 (Evaluation Environmental Impacts), ISO 14043 (Life-Cycle Interpretation), and ISO 14044 (Requirements and Guidelines). According to ISO 14040 (2006), LCA is divided into four stages: Objective and Scope; analysis of life-cycle inventory; life-cycle impact assessment; and interpretation of results.

In studying a biofuel's life cycle, the delineation of system boundaries is fundamentally important and is conducted from two perspectives, considering both the physical boundaries of the productive system and the regression levels of energy and/or mass flows. Physical borders reference sectors of a product's life cycle, specifically relevant characteristic processes.

Many LCAs of biofuels use the "Cradle to Gate" delineation, also referred to as "well to tank" (Capaz 2009; Pieragostini et al. 2012; Tsoutsos et al. 2010; Varanda et al. 2011; Yee et al. 2009). With this delineation, only the energy consumed in the cultivation and processing of biomass and, in some cases, in the distribution of the resulting fuel is considered.

There is a large variety of software that can be used for LCA studies. SimaPro® is frequently used (Capaz 2009; Pieragostini et al. 2012; Tsoutsos et al. 2010), and Eco-Indicator 99 is the most prevalent method use to evaluate production impacts.

Energy efficiency analysis

The mass balance aims to establish energy fluxes, reflected by the net gain from reaction output/input. The efficiency measured by the energy balance describes the amount of energy obtained in relation to the amount of energy used in the system (Heitschmidt et al. 1996).

Approaches to perform energy balances and to determine energy efficiency are important monitoring tools in agriculture, even prior to the use of non-renewable energy sources (de Albuquerque et al. 2007). By accounting for the industrial stage, process analysis can be extended to evaluate the product during most of its life cycle, delivering results that are more reliable. Studies using this process analysis method to verify the process energy balance for production of biodiesel in RS are scarce.

According to Patterson (1996), the four most influential indicators of energy efficiency are the following: thermodynamic; physical–thermodynamic; economical–thermodynamic; and economic. Only the physical–thermodynamic indicator will be used in this study. This choice is in agreement with the objective of the study, provides the advantages of using physical and thermodynamic measurements, and enables the objective measurement of the requirements of consumption for final use. Biodiesel production from various raw materials was evaluated by LCA in three dimensions (environmental, economic, and social) and was compared with fossil fuel production. The LCA included an analysis of the relative output energy/input energy as an important indicator of process sustainability, as suggested by Mata et al. (2011).

The concept of EEA is similar to the energy return on energy invested (EROI), which is the ratio of the usable energy acquired from a particular energy resource to the energy expended to obtain that energy resource (Murphy and Hall 2010). When the EROI of a resource is less than or equal to one, the energy source consumes more energy than it produces.

Methodology

LCA of biodiesel in RS was employed in accordance to the recommendations laid out in ISO 14040 using SimaPro® software, version 7.3 Ph.D., developed by Pre Consultants (Amersfoort, Netherlands) and marketed in Brazil by ACV Brazil (Curitiba, Brazil). Similarly, an energy analysis was performed on the production process.

The biodiesel production process consists of agricultural, transportation, and industrial sectors, and an understanding of these individual sectors is indispensable to understanding the inputs and outputs of the process as a whole. Data collection was based on a theoretical search of relevant organizations that specialize in industrial and agricultural production, whereas practical data were acquired through a survey and technical visits to local industries.

The scope of the study was assumed to be the production of 1.0 (one) ton of biodiesel, which will be used exclusively for energy. Estimates of raw materials and energy consumed are, therefore, related to this amount of production.

1,000 liters (L) of soybean oil was estimated to be required to produce 1,000 liters of biodiesel, so 1.0 ton of biodiesel can, therefore, be produced from 1,018 kg of soybean oil, in agreement with Capaz (2009), with a yield greater than 98 %. However, Penedo et al. (2008) estimated that 1 ton of biodiesel can be generated from 995.73 kg of soybean oil. The average of these values is 1,006.87 kg of soybean oil (or 1,095.61 L). Theoretical oil productivity is 576 kg ha^{-1} year^{-1} or 626.77 L ha^{-1} year^{-1}, so the production of 1,006.87 kg of soybean oil requires an area of 1.75 hectare. With an estimated yield of 3.2 ton ha^{-1} year^{-1}, 1.75 ha produces 5,600 kg of soybeans.

Life-cycle boundaries and inventory allocations

The boundaries adopted in this study are presented in Fig. 2. The assessment was divided into three sectors (agricultural, transportation, and industrial), in other words, the process was studied from “Cradle to Gate” or Well to Gate (WTG). Some assumptions were made to perform the LCA, such as simplifying the inputs and outputs of each stage, choosing the use of utilities and raw materials of greater importance and excluding infrastructure processes (construction). European information and data contained in databases were used only when local data were not available. A more detailed description of the biodiesel production sectors is presented in Appendix.

The qualified and quantified data for such production were allocated in SimaPro® (in terms of mass) from data for the agricultural and industrial sectors (oil extraction, oil refining, and transesterification of the soybean oil). The inventory data used this study are presented in Tables 1, 2, 3, 4, and 5. The results were obtained in terms of environmental damage. To obtain environmental results in SimaPro®, the impact assessment method Eco-Indicator 99 was chosen to provide an unrestricted perspective, based on Contreras et al. (2009), Luo et al. (2009), Cherubini and Strømman (2011), Foteinis et al. (2011), Cavalett et al. (2011), and Nanaki and Koroneos (2012). The results are presented in terms of impact assessment (midpoint).

Energy efficiency analysis

In the EEA, the input and output streams were converted into energy terms from their respective energy coefficients found from relevant references, and the equation for the calculation was adapted from Macedo et al. (2008), according to Eq. (1).

$$\mathrm{EROI} = \left(\frac{\sum \text{energy output}}{\sum \text{fossil energy input}}\right), \tag{1}$$

where

– Energy output represents the energy contained in the final product, including the co-product(s);
– Fossil energy input represents the fossil energy input to the production system.

The EEA considered regression levels 1 and 2, accounting for 90 to 95 % of the process's energy requirements (IFIAS 1978).

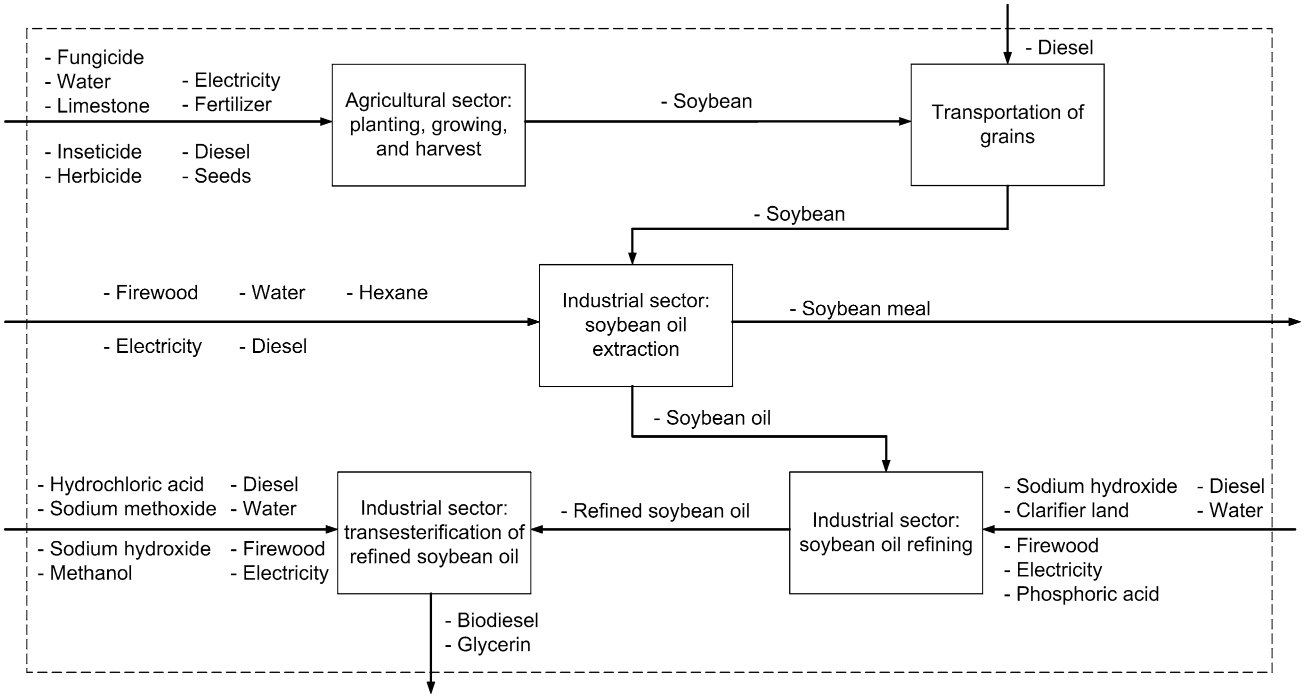

Fig. 2 Boundary of the soybean biodiesel production system

Results and discussion

The input and output flows of each sector considered in the life-cycle analysis of biodiesel production in RS were estimated from collected data. Tables 1, 2, 3, 4, and 5 present the qualified and quantified data in terms of material used in the LCA and in terms of energy assessed in the energy efficiency calculation. Again, the basis was assumed to be production of 1.0 ton of biodiesel.

For environmental analysis, the industrial phases were analyzed individually to identify which flows had a greater potential for impact in each sector. Industrial phases were also evaluated globally. Table 6 presents the greatest impact contributors within each stage.

In the energetic analysis, the calculation of the amount of final energy was performed for the process as a whole. By comparing the stages of biodiesel production in terms of the impact assessment, the agricultural sector was found to be a major contributor to the impact categories, as shown in Fig. 3. Among the eleven categories, the agricultural sector has a higher percentage in six of these categories, followed by the transesterification stage and the transportation stage.

In turn, the refined soybean oil sector has the least impact on the environment, being friendlier to the environment than the other sectors in almost all impact categories.

The LCA showed that in the agricultural stage, the main environmental impacts can be attributed to inputs required to provide better yield and quality of soybeans, such as fertilizers and herbicides.

Phosphorus-rich fertilizers showed the highest impact in four of eleven categories, while herbicides showed the highest percent contribution in more types of impact categories (4 of 11). Weed control is an important practice to ensure high crop yield and may cause environmental problems. Although the use of herbicides for weed control is an indispensable technique, this input has a high potential for environmental impact. Therefore, it is imperative to search for alternative herbicides that are less harmful to the environment.

Diesel accounts for the highest percentage impact in the remaining categories. In the transport step, the results show that diesel has the largest impact percentage in all categories, as the diesel stream is the only stream with real potential for environmental impact. In the industrial sector, diesel had the greatest impact in all categories. In oil refining, diesel again showed significant contributions but in fewer categories (5). Further contributions were attributed to firewood (3), phosphoric acid (2), and sodium hydroxide (1) required for steam generation, degumming, and neutralization, respectively.

In the transesterification step, methanol impacted most LCA categories (5). Further contributions were seen from diesel (3) and sodium methoxide. Ethanol could be a substitute for methanol because it is a renewable feedstock, but operational and reactive issues (need for a greater molar stoichiometric ratio and azeotrope formation with water) are

Table 1 Life-cycle inventory in agricultural sector

Inputs	Mass coefficient		Energy coefficient		Calculated data	
	Specific consumption (amount/unit)	Source	Specific consumption (amount/unit)	Source	Amount[a]	Total energy (J)
Fertilizer (N, P and K)	300 kg/ha/year	Emater (2012)	Nitrogen—56.5 MJ/kg	Capaz (2009) based in model EBAMM and GREET	525.00 kg	5E+09
			Phosphorus—7.5 MJ/kg	Capaz (2009) based in model EBAMM and GREET		
			Potassium—7 MJ/kg	Seabra (2008)		
Fungicide (Opera, Standak and Talstar)	2.17 kg/ha/year	Emater (2012)	216.0 MJ/kg	Taki et al. (2012)	3.80 kg	8.21E+08
Herbicide glyphosate	3 L/ha/year	Emater (2012)	418.6 MJ/kg	Pimentel and Patzek (2005)	5.25 L (8.98 kg)	3.76E+09
Insecticide (Dimilin and Permitrina)	0.43 kg/ha/yr	Emater (2012)	358.0 MJ/kg	Nogueira (2011)	0.75 kg	1.79E+08
Limestone	2,000 kg/ha/year	Nogueira (2011)	0.1 MJ/kg	Nogueira (2011)	3,500.0 kg	3.5E+08
Water	1,500 L/ha/year	Local data	$4{,}940 \times 10^{-3}$ MJ/kg	Odum (1996)	2,625.00 L	1.30E+07
Diesel	50 L/ha/year	Local data	47.72 MJ/L	Pimentel and Patzek (2005)	87.50 L	4.18E+09
Seeds	50 kg/ha/year	Cederberg and Flysjö (2004); Nogueira (2011)	33.46 MJ/kg	Pimentel and Patzek (2005)	87.50 kg	2.93E+09
Electricity	34 kWh/ha/year	Cavalett (2008)	3.6 MJ/kWh	–	59.50 kWh	2.14E+08
Output					Amount	Total energy (J)
Soybean	3,200 kg/ha/yr	Emater (2012)	39.575 MJ/kg	Knothe et al. (2006)	5,600.00 kg	2.17E+11

[a] Amount needed in the production of 1.0 ton of biodiesel

Table 2 Life-cycle inventory in transportation sector

Inputs	Mass coefficient		Energy coefficient		Calculated data	
	Specific consumption (amount/unit)	Source	Specific consumption (amount/unit)	Source	Amount[a]	Total energy (J)
Soybean	3,200 kg/ha year	Emater (2012)	39.575 MJ/kg	Knothe et al. (2006)	5,600.00 kg	2.17E+11
Diesel	2.5 km/L (Truck capacity of 10 ton)	Average distance of 140 km	47.72 MJ/L	Pimentel and Patzek (2005)	55.93 L	2.67E+09
Outputs					Amount	Total energy(J)
Soybean	3,200 kg/ha year	Emater (2012)	39.575 MJ/kg	Knothe et al. (2006)	5,600.00 kg	2.17E+11

barriers for ethanol compared to methanol. Although methanol consumption is smaller, biodiesel yield using ethanol is higher. However, issues of supply, logistics, and operational security are the most relevant factors (Khalil 2006).

Methanol is the most widely used because of its low cost in most countries and its physical and chemical advantages, including polarity, shorter chemical chain, faster reaction with triacylglycerol, and easy dissolution of the basic catalyst (Ma and Hanna 1999). The use of methanol implies a high potential for environmental impact, although Castanheira et al. (2014) state that the environmental impacts from the two routes are similar, with difference <10 %.

Table 3 Life-Cycle Inventory in Industrial sector: soybean oil extraction

Inputs	Mass coefficient		Energy coefficient		Calculated data	
	Specific consumption (amount/unit)	Source	Specific consumption (amount/unit)	Source	Amount[a]	Total energy (J)
Soybean	3,200 kg/ha/yr	Emater (2012)	39.575 MJ/kg	Knothe et al. (2006)	5,600.00 kg	2.17E +11
Electricity	0.0299 kWh/kg soybean	Dorsa (2000)	3.6 MJ/kWh	–	167.44 kWh	6.02E +08
Hexane	2 L/ton soybean (~1.36 kg/ton soybean)	EPE (2005)	22.5 MJ/kg	Sheehan et al. (1998)	7.62 kg	1.71E +08
Firewood	62.5 kg/ton soybean	Capaz (2009)	12.98 MJ/kg	BEN (2012)	0.70 m^3 (350 kg)	4.54E +09
Water	0.000719 m^3/kg soybean	Dorsa (2000)	4,940 J/kg	Odum (1996)	4.03 m^3 (4,030 L)	2.00E +07
Diesel	0.0179 kg/kg soybean	Dorsa (2000)	47.72 MJ/L	Pimentel and Patzek (2005)	119.33 L	5.69E +09
Outputs					Amount	Amount (J)
Soybean oil	0.18 kg/kg	Penedo et al. (2008), Capaz (2009)	39.60 MJ/kg	Domalski et al. (1986)	1,006.87 kg	3.98E+10
Soybean meal	0.79 kg/kg	Penedo et al. (2008), Capaz (2009)	17.2 MJ/kg	Baker et al. (2014)	4,424.0 kg	7.61E+10

Table 4 Life-cycle inventory in industrial sector: soybean oil refining

Inputs	Mass coefficient		Energy coefficient		Calculated data	
	Specific consumption (amount/unit)	Source	Specific consumption (amount/unit)	Source	Amount[a]	Total energy (J)
Soybean oil	Estimated	Based in Penedo et al. (2008), Capaz (2009)	39.60 MJ/kg	Domalski et al. (1986)	1,006.87 kg	3.98E+10
Electricity	0.0126 kWh/kg soybean oil	Dorsa (2000)	3.6 MJ/kWh	–	12.67 kWh	4.50E+07
Diesel	0.0036 kg/kg soybean oil	Dorsa (2000)	47.72 MJ/L	Pimentel and Patzek (2005)	4.32 L	206E+08
Firewood	62.5 kg/ton soybean	Capaz (2009)	12.98 MJ/kg	BEN (2012)	0.70 m^3	4.54E+09
Water	0.000817 m^3/kg soybean oil	Dorsa (2000)	4,940 J/kg	Odum (1996)	0.82 m^3 (820 L)	4.05E+06
Phosphoric acid (H_3PO_4)	0.0005 kg/kg soybean oil	Dorsa (2000)	10.32 MJ/kg	Spinelli et al. (2013)	0.50 kg	5.16E+06
Sodium hydroxide (NaOH)	0.00448 kg/kg soybean oil	Dorsa (2000)	19.95 MJ/kg	Sheehan et al. (1998)	4.51 kg	9.0E+08
Clarifier land	0.0035 kg/kg soybean oil	Dorsa (2000)	–	–	3.52 kg	–
Outputs					Amount	Amount (J)
Refined soybean oil	Estimated	Based in Penedo et al. (2008); Capaz (2009)	39.60 MJ/kg	Domalski et al. (1986)	1,006.87 kg	3.98E+10

The question to be discussed is whether environmental factors prevail over industrial/economic factors.

The fact that diesel is the largest contributor to the ozone layer and respiratory organics categories in all stages of the biodiesel production process is evidence of diesel's high pollution potential and a strong argument for a gradual reduction in its use.

In the EEA, quantification of waste, effluents, and emissions was ignored because these values were not directly involved in the energy efficiency calculation and

Table 5 Life-Cycle Inventory in Industrial sector: transesterification of soybean oil

Inputs	Mass coefficient		Energy coefficient		Calculated data	
	Specific consumption (amount/unit)	Source	Specific consumption (amount/unit)	Source	Amount[a]	Total energy (J)
Refined soybean oil	Estimated	Based in Penedo et al. (2008), Capaz (2009)	39.60 MJ/kg	Domalski et al. (1986)	1,006.87 kg	3.98E+10
Diesel	0.0537 kg/kg soybean oil	Fortenbery (2005), Cavalett (2008)	47.72 MJ/L	Pimentel and Patzek (2005)	64.37 L	3.07E+09
Methanol	0.187 L/kg soybean oil	Fortenbery (2005); Cavalett (2008)	39.3 MJ/kg	Sheehan et al. (1998)	188.28 L (149 kg)	5.86E+09
Sodium methoxide	0.0107 L/kg soybean oil	Fortenbery (2005), Cavalett (2008)	39.1 MJ/kg	Sheehan et al. (1998)	12.85 L (16.70 kg) (in excess)	6.52E+08
Electricity	0.000882 kWh/kg soybean oil	Fortenbery (2005), Cavalett (2008)	3.6 MJ/kWh	–	0.89 kWh	3.20E +06
Water	0.511 m^3/kg soybean oil	Fortenbery (2005), Cavalett (2008)	4,940 J/kg	Odum (1996)	514.51 m^3 (514.510 L)	2.54E +09
Hydrochloric acid	0.00794 kg/kg soybean oil	Calculated in this work	21,03 MJ/kg	Sheehan et al. (1998)	8.00 kg	1.68E+08
Sodium hydroxide	0.00418 kg/kg soybean oil	Dorsa (2000)	19.95 MJ/kg	Sheehan et al. (1998)	4.21 kg	8.39E+08
Firewood	62.5 kg/ton soybean	Capaz (2009)	12.98 MJ/kg	BEN (2012)	0.70 m^3	4.55E+09
Outputs					Amount	Amount (J)
Biodiesel	Estimated	Based in Penedo et al. (2008), Capaz (2009)	39.95 MJ/kg	Sheehan et al. (1998)	1,000.00 kg	~4E+10
Glycerin	10-14 % of biodiesel production	Penedo et al. (2008), Capaz (2009)	16.20 MJ/kg	Mourad and Walter (2011)	113.64 kg	1.84E +09

Table 6 Principal streams and their contributions to the impact categories

Sector/impact categories	Agricultural	Transport	Extraction	Refine	Transesterification
Carcinogens	Herbicides: 53.58 %	Exclusively to diesel in all categories	Diesel: 75.98 %	Phosphoric acid: 81.82 %	Sodium methoxide: 46.14 % Methanol: 46.22 %
Respiratory organics	Diesel: 54.71 %		Diesel: 87.51 %	Diesel: 73.42 %	Diesel: 77.04 %
Respiratory inorganics	Fertilizer (P): 74.59 %		Diesel: 78.70 %	Firewood: 57.01 %	Sodium methoxide: 30.10 %
Climate change	Fertilizer (P): 54.52 %		Diesel: 84.25 %	Sodium hydroxide: 38.73 %	Sodium methoxide: 37.88 %
Radiation	Herbicides: 46.20 %		Diesel: 87.22 %	Diesel: 48.59 %	Methanol: 49.16 %
Ozone layer	Diesel: 53.28 %		Diesel: 99.16 %	Diesel: 92.48 %	Diesel: 91.39 %
Ecotoxicity	Herbicides: 38.09 %		Diesel: 94.30 %	Diesel: 55.56 %	Sodium methoxide: 26.14 % Methanol: 25.76 %
Acidification/ Eutrophication	Fertilizer (P): 78.10 %		Diesel: 80.64 %	Firewood: 62.65 %	Methanol: 31.67 %
Land use	Diesel: 37.51 %		Diesel: 95.27 %	Phosphoric acid: 73.84 %	Methanol: 94.77 %
Minerals	Herbicides: 53.53 %		Diesel: 89.24 %	Firewood: 72.15 %	Methanol: 67.52 %
Fossil fuels	Fertilizer (P): 51.10 %		Diesel: 90.70 %	Diesel: 56.24 %	Diesel: 54.82 %

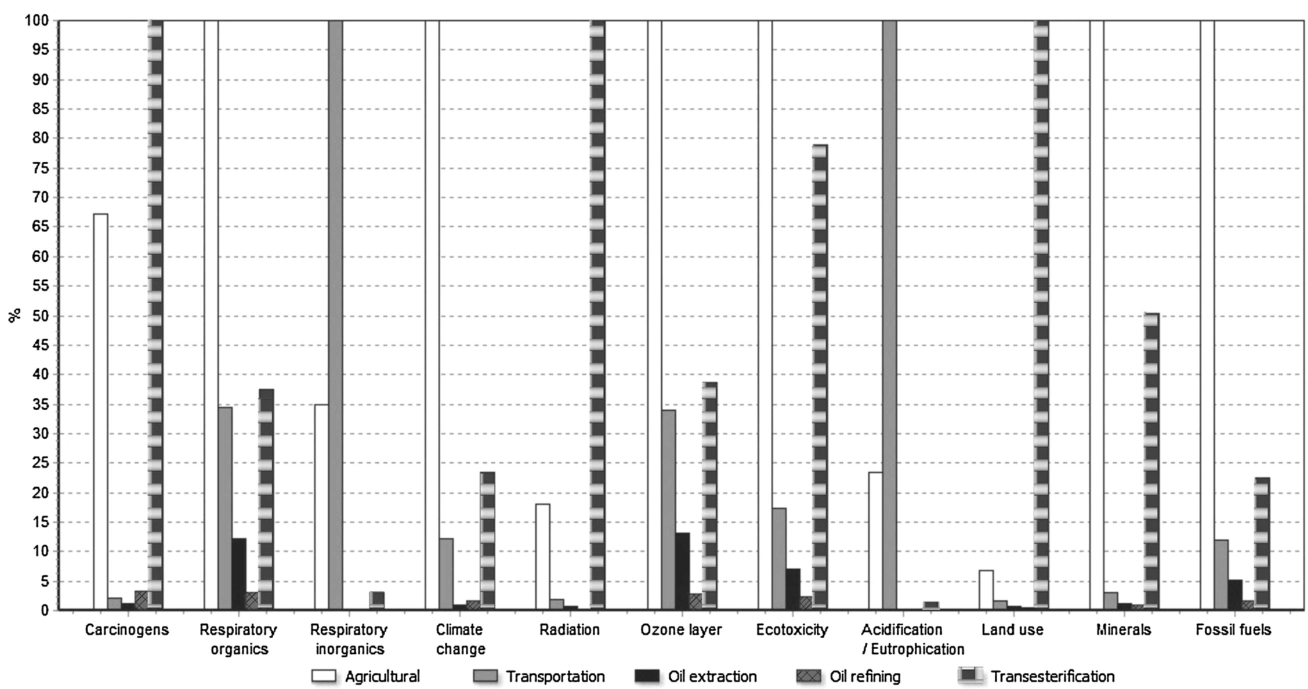

Fig. 3 Comparison between process sectors (impact assessment–midpoint)

are considered losses resulting from non-conversion into useful energy (entropic losses of system). The energy input in the clarifier used in oil refining was unable to be converted, but this energy input was believed not to significantly influence the results when comparing energy values using similar feedstocks.

Table 7 EROI and energy input (%, per sector) for the production of biodiesel from soybean in the alkaline methyl route

Reference	EROI[a]	Energy input (% of total input)	
		Agricultural	Non-agricultural[a,b]
Capaz (2009)	4.30	48,6	51,4
Soares et al. (2008)	3.21	76,3	23,7
Empresa de Pesquisa Energética (2005)	2.50	69,8	30,2
Sheehan et al. (1998)	3.20	48,4	51,6
Hill et al. (2006)	1.93	63,4	36,6
This work	3.08	52,5	47,5

[a] Considering co-products allocation

[b] Including transportation and industrial energy inputs

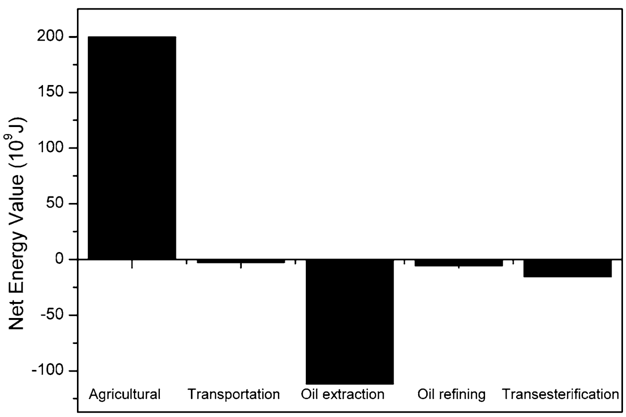

Fig. 4 Net Energy Value for the steps in the production of 1.0 ton of soybean biodiesel

The biodiesel process EEA shows an EROI of 3.08, implying a surplus of energy. In other words, energy production was greater than consumed. This finding is consistent with the results shown in Table 7, which compares studies based on the production of biodiesel from soybeans using methanol as the reagent in the alkaline route. Diesel was the major input along the process, accounting for 7.3 % of total input, followed by firewood (6.3 %), methanol (2.7 %), and fertilizers (2.3 %). Combining the EEA and LCA results, where diesel was the most damaging stream, it is possible to argue for the partial or total replacement of diesel with biodiesel to reduce environmental damage and energy demand.

The energy assessment in each production sector, presented in Fig. 4, shows that the agricultural sector is the only energetically positive step, with an EROI of 12.43. The most energetically intensive step was in oil extraction, mainly because of firewood and diesel consumption (almost 93 % of the total in this step), resulting in an EROI of 0.51. Oil extraction step accounts for 84 % of the energy input in industrial sector, requiring special attention to reduce energy consumption and to raise the EROI of biodiesel.

In this study, the share of soybean meal in the EROI was almost 64 % of the total (almost two times the energy in biodiesel), more than that presented in the work of Hill et al. (2006) (33.5 %), while the biodiesel share was about the same (near 1.0). The EROI values for biodiesel production found in the literature (Table 7) have great variability because of the different climate conditions, techniques, and raw materials that affect soybean cultivation or energy inputs along the process. The studies presented in Table 7 show a trend of equal division of energy input between agricultural and non-agricultural (transportation and industrial) sectors, although the agricultural sector tends to be more energy intensive. In general, the higher the share of agricultural sector in total energy input the lower will be the EROI of the process. This indicates that energy input in non-agricultural sectors does not vary substantially with the country where biodiesel is produced.

Conclusions

The results showed that, in the agricultural stage, fertilizers rich in phosphorus as well as herbicides are responsible for much of the impact to the environment, while the grain transportation stage indicated that the use of diesel as fuel for trucks resulted in higher damage in all categories considered by the Eco-Indicator 99 assessment method.

Diesel consumption has a principal responsibility for environmental impact during soybean oil extraction, while the impact from refining soybean oil varied according to the types of impact. Impact from firewood consumption of firewood is emphasized, as this fuel is widely used in steam generation, and the extraction process can cause major impact. Additionally, phosphoric acid, sodium hydroxide, and diesel contribute significantly to environmental impact in the refining stage.

In transesterification, sodium methoxide and methanol are represented significantly in the impact categories. The use of diesel impacts all of the industrial stages, mainly in relation to respiratory organics, ozone layer, and fossil fuels, contributing no less than 50 % of the impact.

Comparing the process as a whole, the stage with potentially more pollution to the environment was the agricultural stage. The analysis of this sector suggests that a bolder approach may be necessary to promote a reduction in pollution. Evaluating only the industrial stages, transesterification of refined oil has greater potential for pollution.

In terms of energy output, the production of biodiesel and co-products in RS generates 3.08 times energy than it is consumed in the process. The agricultural and non-agricultural sectors have similar share in energy input along the biodiesel production, whereas agricultural remains as the key sector to ensure a positive energy balance. These results prove the importance of this biofuels to supply the energy demand of RS and Brazil.

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Appendix

The LCA and EEA performed in this study considered the boundaries defined in Fig. 2. These boundaries comprise the Agricultural, Transportation, and Industrial sectors, according to "Cradle to Gate" or WTG delineation.

Agricultural sector

The agricultural sector is shown in Fig. 5. The flows of this step include soil preparation, seeding, cultivation, and harvest. In the soil preparation step, a series of operations are necessary, including plowing, grading, and ground leveling using tractors and plows. Soil acidity must then be adjusted (liming), and the soybean is planted and cultivated. Crop quality is maintained by applying fertilizers, fungicides, and herbicides. The final step is mechanized harvest.

Transportation sector

After harvest, soybeans are transported by truck to the storage location in farms or cooperatives and subsequently transported to the processing industry.

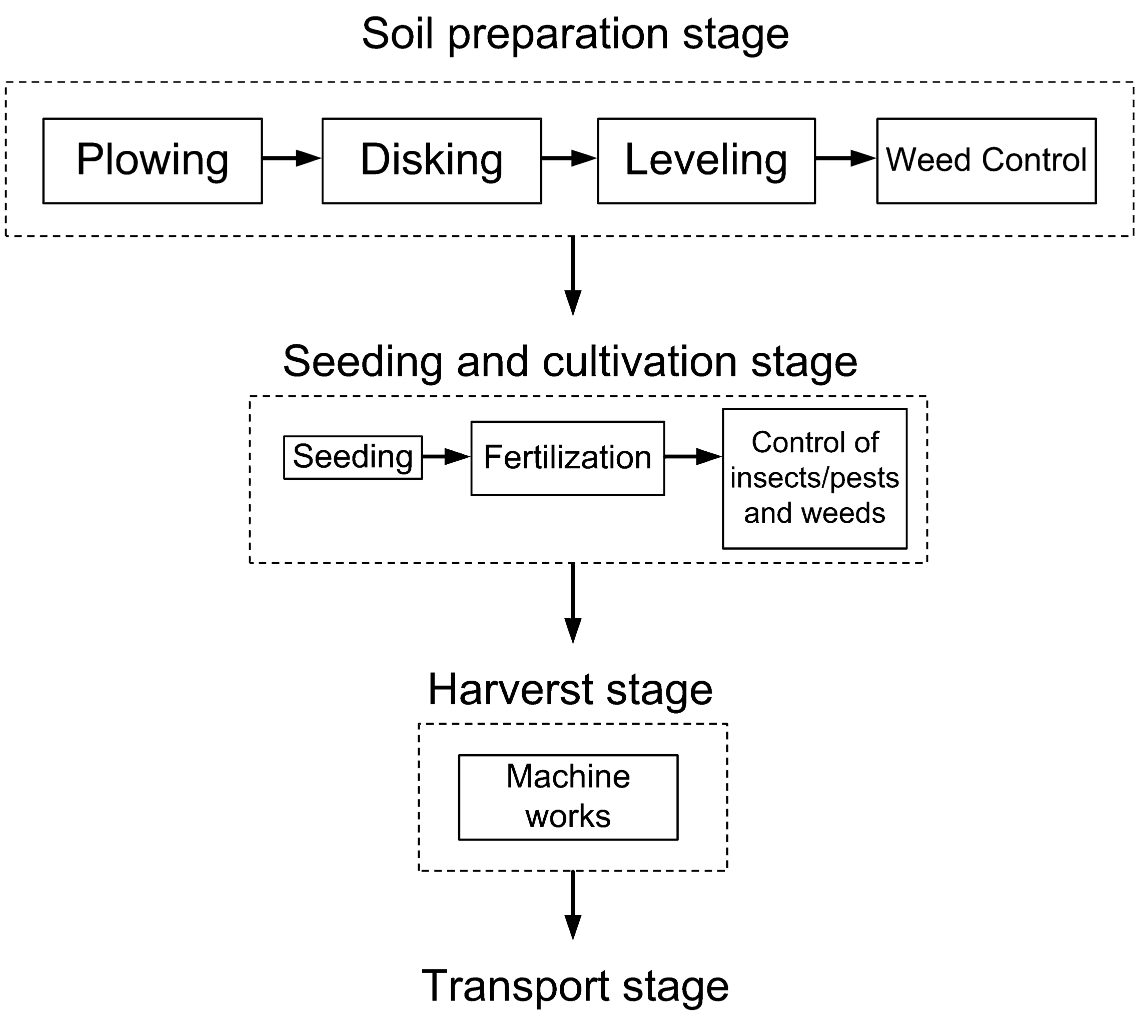

Fig. 5 Agricultural sector flowchart

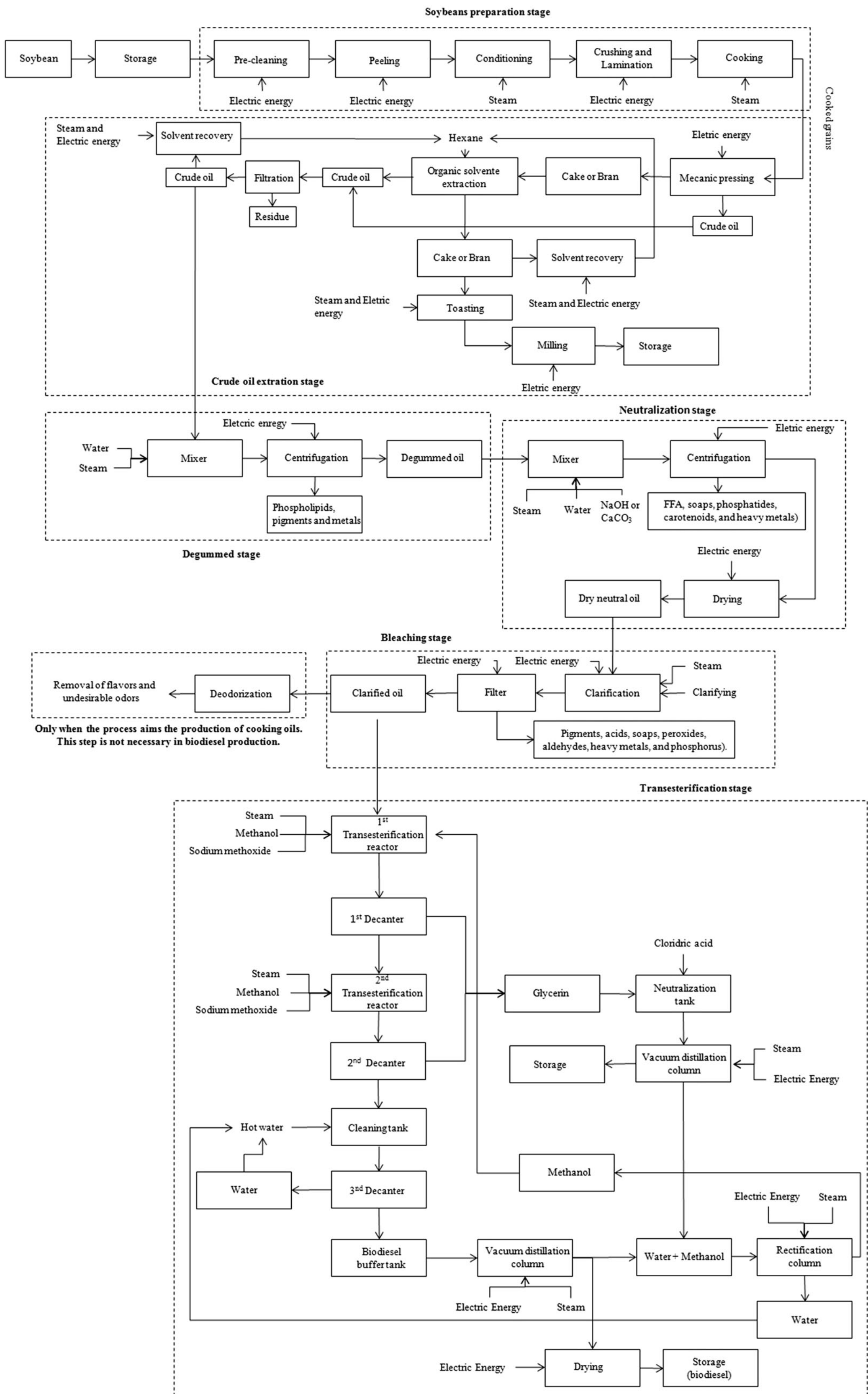

Fig. 6 Industrial sector flowchart

Industrial sector

In RS, the grain processing industries are integrated, that is, the industrial unit consists of sectors for the extraction, refining, and transesterification of soybean oil. Therefore, the analysis of the industrial sector was divided in these three sectors.

Soybean oil extraction

The initial step in the industrial sector is the extraction of soybean oil, commonly called crude soybean oil. Before extraction, the grains pass through preliminary steps (storage and preparation of grain) needed to provide greater oil extraction efficiency.

The grain preparation step consists of storage and precleaning, peeling, conditioning (heating the pulp to facilitate oil extraction), crushing and lamination (to increase grain surface area), and cooking (disruption of cell walls to facilitate oil extraction) (Mandarino and Roessing 2001). These steps are shown in Fig. 6.

Next, the grains enter into the oil extraction step (see Fig. 6). Oil is extracted mechanically, followed by extraction with organic solvent (usually hexane). The cake that leaves the press is subjected to the solvent, which removes residual oil. The solvent is separated from the oil through distillation, and the recovered oil is mixed with the crude oil removed from pressing. This mixture is filtrated to eliminate impurities arising from the mechanical process. The soybean meal or cake has low oil content and is milled and stored in silos.

Soybean oil refining

The refining step makes the oil suitable for transesterification, that is, with acceptable levels of free fatty acids, moisture, colloidal substances, proteins, phosphatides, and other impurities. Vegetable oil with high purity is required to avoid problems such as hydrolysis and saponification reactions that result in lower biodiesel yields and cause problems in the separation of biodiesel and glycerin.

The steps in the refining of crude soybean oil (see Fig. 6) are divided into degumming or hydration (removal of phosphatides such as lecithin), neutralization (to eliminate impurities and free fatty acids from the "degummed oil"), and clarifying (adsorption of pigments contained in "neutralized oil").

Transesterification of soybean oil

The transesterification of refined oil (see Fig. 6) occurs in the presence of methanol (excess) and sodium methoxide (catalyst), producing biodiesel and glycerin. Reagents are introduced into a continuous stirred reactor with a mean temperature of 60 °C and under atmospheric pressure. The products are sent to a decanter to separate biodiesel (light phase) from glycerin (heavy phase). Each phase contains unreacted oil (an insignificant amount), methanol, and catalyst. The heavy phase has a greater affinity for methanol and catalyst, while the lighter phase has greater affinity for unreacted oil. The heavy phase is neutralized with hydrochloric acid to stop the reaction, adjust its pH, and separate the catalyst, which is recovered by washing. The mixture of glycerin, water, and methanol is subjected to vacuum distillation to separate methanol and water.

The light phase is washed with hot water to remove free fatty acids and any remaining catalyst present in the biodiesel. The wash water is subjected to decantation to separate the biodiesel. The biodiesel proceeds to vacuum distillation to separate water and methanol contained within it. The biodiesel is then cooled and filtered (filter press), and dry biodiesel is then stored in tanks. Methanol and water recovered from biodiesel (light phase) and glycerin (heavy phase) are separated in a rectification column, and then reused in the process.

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