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Comparison of the Productive Viability of Biodiesel by Methanolic and Ethanolic Transesterification

Erich Potrich[1]*, Larissa Souza Amaral[2] and Thaís Cereda Ravasi[3]
[1]*State University of Amapá – UEAP, Macapá – AP, Brazil;*
[2]*State University of Minas Gerais – UEMG, Frutal – MG, Brazil;*
[3]*Centro Universitário Central Paulista – Unicep, São Carlos – SP, Brazil.*
Corresponding Author: erich.potrich@ueap.edu.br*

ABSTRACT : *Biodiesel is the second most produced biofuel in Brazil, while ethanol is the first. Although biodiesel is a biofuel, methanol, which comes from natural gas, is actively involved in its production. Ethanol could replace methanol in the production process. The present work carried out the economic viability, location and risk analysis for the production of biodiesel by methanol and by ethanol in Brazil. The results show that, depending on the price of raw materials, ethanol can have the same economic viability as methanol, or be only 3.9% less advantageous. Besides that, ethanol is safer and less toxic than methanol.*

KEYWORDS: *biodiesel; feasibility analysis; economic viability; location analysis; risk analysis.*

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I. INTRODUCTION

Brazil is the second largest producer of both ethanol and biodiesel, with the USA the largest producer. In 2019 Brazil produced 5.9 million m³ of biodiesel. For ethanol, Brazil produced 35.3 million m³ [1]. Currently, 12% biodiesel is mixed in diesel, and 27% anhydrous ethanol in gasoline.

The biodiesel production process may be by esterification or transesterification. Esterification consists of the reversible reaction of a fatty acid with an alcohol producing ester (biodiesel) and water. The transesterification, which is the most used method, is a chemical reaction between a triglyceride (fatty oil) and three molecules of alcohol, producing three molecules of esters and one molecule of glycerol [2]. Since transesterification is a reversible reaction, the reactor is fed with excess alcohol to displace the reaction for the formation of products, usually six moles of alcohol are fed to each mole of oil [3]. In addition to the price, other advantages of transesterification are the production of a fatty acid ester with physical characteristics much closer to that of diesel and the production process is simpler [4-6].

The most commonly used alcohols for transesterification are methanol and ethanol. While methanol is mainly obtained by methane from natural gas, ethanol in Brazil is obtained from the fermentation of the sugarcane juice. The reaction with ethanol is more complicated because any presence of water in the process causes the yield of biodiesel to decay, being necessary to work only with anhydrous ethanol [7] The methyl route produces 33% more greenhouse gases compared to the ethanol route [8].

A way to compare methanol and ethanol is by feasibility study, which are tools in which organizations rely to decide their strategies. Some steps in the feasibility study process are: market study, size and location study, engineering, cost and revenue analysis, and economic viability assessment [9].

The biodiesel market is already well established, and changing methanol to ethanol in the production stage would not entail any loss in as well as engineering for the production of biodiesel is the same for both routes. The aim of this study is to analyze the economic feasibility, location and risk comparing biodiesel production via methanolic and ethanolic route.

II. METHODOLOGY

Economic Feasibility Analysis

The biodiesel production process is the same regardless of the type of alcohol to be used in the transesterification step, methanol or ethanol. No industrial equipment or method is modified when processing methanol or ethanol.

The economic analysis developed by this work considered only the differences between methanol and ethanol in the industrial process, which is the purchase price and the process of evaporation of them. The values obtained in this work were in Brazilian Real and later converted into US dollar for the average of the last 5 years (oct/15 – set/20), the conversion value used was R$ 1.00 ≈ US$ 0.26.

According to PMBOK [10], cost estimation is a process that estimates the monetary resources needed to execute the activities of a project. The activity at issue here is the production of one liter of biodiesel.

A cost estimating tool is the three point estimate, which are: the most probable point (cM), the optimistic point (cO) and the pessimistic point (cP). The expected cost (cE) can be calculated by means of the triangular distribution given by Equation 1 [10]:

$$cE = (cM + cO + cP)/3 \tag{1}$$

The most probable cost used for this work was based on the last set of data provided by the National Agency of Petroleum, Natural Gas and Biofuels of Brazil (ANP - Agência Nacional do Petróleo, Gás Natural e Biocombustíveis) [1]. The optimistic cost was based on the smaller price difference between methanol and ethanol in the last 5 years. The pessimistic cost was based on the largest price difference between methanol and ethanol in the last 5 years.

The price variation of methanol and anhydrous ethanol over time can be seen in ANP [1]. In October 2015, there is the closest price between methanol and ethanol. November 2016 presents the biggest price difference between methanol and ethanol. In July 2017 is the last data of the chart. However, for the values to be more correct, the inflation between the periods must be considered. Based on the Brazilian Consumer Price Index the values were adjusted for September 2020 [11]. Based on these three periods was constructed Table 1 which analyzed the prices of raw materials and sale of biodiesel. In Table 1, the values with negative signs mean expenses in the purchase of raw materials, while values with positive signs mean gains in the sale of products.

Table 1. Purchase and sale prices of raw materials at three points (cO, cP and cM) with the correction of inflation.

		cO	**cP**	**cM**
		October 2015	November 2016	July 2017
			Price (US$/L)	
Reaction with methanol	Soy oil	-0.69	-0.79	-0.62
	Methanol	-0.37	-0.26	-0.29
	Glycerol	+0.56	+0.56	+0.62
	Methyl Biodiesel	+0.89	+0.86	+0.72
Reaction with ethanol	Soy oil	-0.69	-0.79	-0.62
	Ethanol	-0.45	-0.62	-0.43
	Glycerol	+0.56	+0.56	+0.62
	Ethyl Biodiesel	+0.89	+0.86	+0.72

As the reaction is in excess of alcohol, 3 moles of alcohol left over for each mole of oil fed, it is necessary to evaporate this alcohol to recover it to react again and make the biodiesel purer. This evaporation stage is the most expensive stage of production, in terms of electricity demand, since a large heat demand is required to evaporate all excess alcohol. The amount of heat (Q) required to evaporate the alcohol is the heat required to raise the mass substance (m) from the ambient temperature ($T_{ambient}$ = 25 ^oC) to the boiling point ($T_{boiling}$) and evaporate it completely.

In Brazil the value of the electricity price (US$/kWh) changes for each flag color. The tariffs for electric energy began to be valid in January 2015 and indicate whether or not there will be an increase in the price of energy to be passed on to the final consumer, depending on the conditions of electricity generation. The green flag indicates favorable conditions of power generation and that there will be no increase in the price of energy. The red flag level 2 indicates the worst conditions for the generation of energy, resulting in a greater increase in the price of electric energy. In October 2015 was red flag level 1 (US$/kWh 0.10776), in November 2016 and July 2017 was yellow flag (US$/kWh 0.10251) [12].

There are also other operating costs in a biodiesel industry, such as the separation and subsequent purification of biodiesel and glycerol. These costs were not considered in this study because they are small in relation to the costs of raw material, besides that they do not differ between the methanolic and ethanolic routes [13-14].

The economic analysis was made based on the three periods (cO, cP and cM). The analysis only considered the price of raw materials and the price of electric energy to evaporate the alcohols to produce one liter per hour of biodiesel. This analysis was done to see if a biodiesel plant operating with ethanol instead of methanol would have a significant drop in its profit.

Location Analysis

In Brazil, 80% of the transportation of raw materials and products is carried out by road transport. This great dependence on the road network in Brazil and its poor quality of infrastructure leads to an increase in expenses. According to a survey carried out by the Brazilian National Confederation of Transport [15], in 2015, 57% of the road network analyzed has deficiencies in its general condition, which increase transportation costs by 25%.

According to the Union of Freight Transport and Logistics Companies in the State of Rio Grande do Sul [16], for each ton of solid bulk material transported there is an average additional cost of US$ 3.82 for a journey of only 25 km, reaching a value of US$ 312.00 per ton transported for a route of 6 thousand km. The price of diesel fuel being responsible for half that amount.

The economic viability of ethyl biodiesel production would be greatly facilitated by the integrated production of biodiesel and ethanol in the same plant, as well as these industrial plants located in the producing regions of raw material. As a result, the industry would not suffer from the impact of the oscillation in the market price of ethanol and, above all, from the impact of transport prices.

These integrated biorefineries would naturally be allocated where the main raw materials in each sector were produced in adjacent areas. The main raw materials currently used to produce biodiesel in Brazil are soybean oil, responsible for 68.0% of production, while the raw material for Brazilian ethanol is sugarcane [1]. The location analysis was carried out in regions where soy and sugarcane are produced.

Risk Analysis

PMBOK describes the risk as an event or uncertain condition that if it occurs will have an effect on the scope, on the schedule, on the cost or on the quality of the process [10].

In the chemical area, there are some tools that help in risk analysis, such as the Hommel's diagram, the potential health effects, the median lethal dose (LD_{50}) and the lowest published lethal dose (LD_{LO}). With these data gives to build the Preliminary Analysis of Danger (APP).

The Hommel's diagram is a symbol used to show the risks that a particular chemical can present. In this diagram, squares are used that express the types of risk in degrees that vary from 0 to 4, each one specified by a color (white, blue, yellow and red), representing, respectively: specific risks, health risk, reactivity and flammability [17-18].

Potential health effects are a qualitative analysis of the effects that a particular chemical can have on humans being inhaled, ingested, in contact with the skin or the eyes, or if there is chronic exposure.

The median lethal dose and the lowest published lethal dose are life-threatening quantitative analyzes. The median lethal dose (LD_{50}) is the required dose of a given substance to cause the death of 50% of a given population of animals. The lowest published lethal dose (LD_{LO}) is the lowest dosage of a given substance reported in the scientific literature in which the individual died. LD_{50} and LD_{LO} are generally measured in milligrams of substance per kilogram of body mass of the individuals tested. Both are used as indicators of acute toxicity of a substance, because the higher the dose that will be lethal, the less toxic the substance is considered [19-20].

The preliminary hazard analysis is a qualitative technique used to identify the hazards present in industrial units, and their classification in terms of frequency of occurrence (freq.), severity (sev.) and risk (freq.x sev.). The frequency is measured on a scale from A (extremely remote) to E (frequent), severity is measured from I (negligible) to IV (catastrophic), and the risk is measured from 1 (negligible) to 5 (critical) [21-22].

III. RESULTS AND DISCUSSION

Economic Feasibility Analysis

Considering the production of one liter of biodiesel and information taken from literature [23-25], the amount of heat of evaportion required for methanol is of 0.032 kWh, while for ethanol 0,036 kWh is the quantity of heat required. With these required heat values, the cost of evaporation is less than US$ 0.01. This value is the same for different flags and different alcohols. With this, the cost of evaporation is not a relevant cost close to the costs of raw materials. Based on the data collected so far, Table 2 was constructed with the calculation basis of one liter of biodiesel produced.

Table 2. Profit for the production of biodiesel by analyzing only raw material prices and the evaporation stage for three different points (cO, cP and cM).

		cO	**cP**	**cM**
		October 2015	November 2016	July 2017
		Value per liter of biodiesel produced (US$)		
Reaction with methanol	Soy oil	-0.64	-0.73	-0.57
	Methanol	-0.04	-0.03	-0.03
	Glycerol	+0.04	+0.04	+0.04
	Methyl Biodiesel	+0.89	+0.86	+0.72
	Total cost	0.69	0.77	0.61
	Profit	0.25	0.14	0.16
Reaction with ethanol	Soy oil	-0.61	-0.70	-0.55
	Ethanol	-0.07	-0.10	-0.07
	Glycerol	+0.04	+0.04	+0.04
	Ethyl Biodiesel	+0.89	+0.86	+0.72
	Total cost	0.69	0.80	0.62
	Profit	0.24	0.10	0.15

The values in Table 2 are not the actual profits of the industry, there are still many other costs to be added, but already has an idea of how the profit behaves in each period of time. During the past five years, November 2016 was less favorable to produce biodiesel from ethanol, with a profit drop of 4 cents compared to methanol, for every liter of biodiesel produced. In October 2015 the production price for each liter of biodiesel was practically the same using both methanol and ethanol. A large industry could increase profits by using the reaction with ethanol through the sale of carbon credits, which is around € 26.9 for each ton of CO_2 that is no longer being released to the environment (average price on September 30th).

In October of 2015, although the price of the liter of ethanol was 23.33% higher than the price of the liter of methanol, the price of the biodiesel production cost, based only on the values of the raw material, was exactly the same. As early as November 2016, the price of the liter of ethanol was 139.13% higher, but the cost per liter of biodiesel was only 3.90% higher for the ethanolic route. Finally, in July 2017, ethanol was 50% more expensive than methanol, but the price difference was only 1.64%. As the process using ethanol requires less soybean oil compared to the process using methanol, raising the value of soybean oil would increase the viability of the ethanol route.

Using Equation 1, the expected cost for methanol is US$ 0.69 and for ethanol is US$ 0.70. With the analysis of the three points, the cost of biodiesel production by the ethanol route is 1.45% higher compared to the methanolic route. One solution to reduce this difference would be if ethanol and biodiesel were produced in the same plant. With this, there would be less dependence on the market and its price oscillation, and could perhaps make it more profitable to produce biodiesel through the ethanolic route.

Location Analysis

The mesoregions that simultaneously produce soybean and sugarcane are: pioneer north of Paraná (PR), Assis region in the state of São Paulo (SP), Minas Gerais (MG) triangle, Mato Grosso do Sul (MS) southwest, Goiás (GO) south, and on the regional border between the south-central meso and southwest meso of Mato Grosso (MT). These same mesoregions share biodiesel and ethanol production units [1, 26-27]. Figure 1 shows these regions in blue on the map of Brazil.

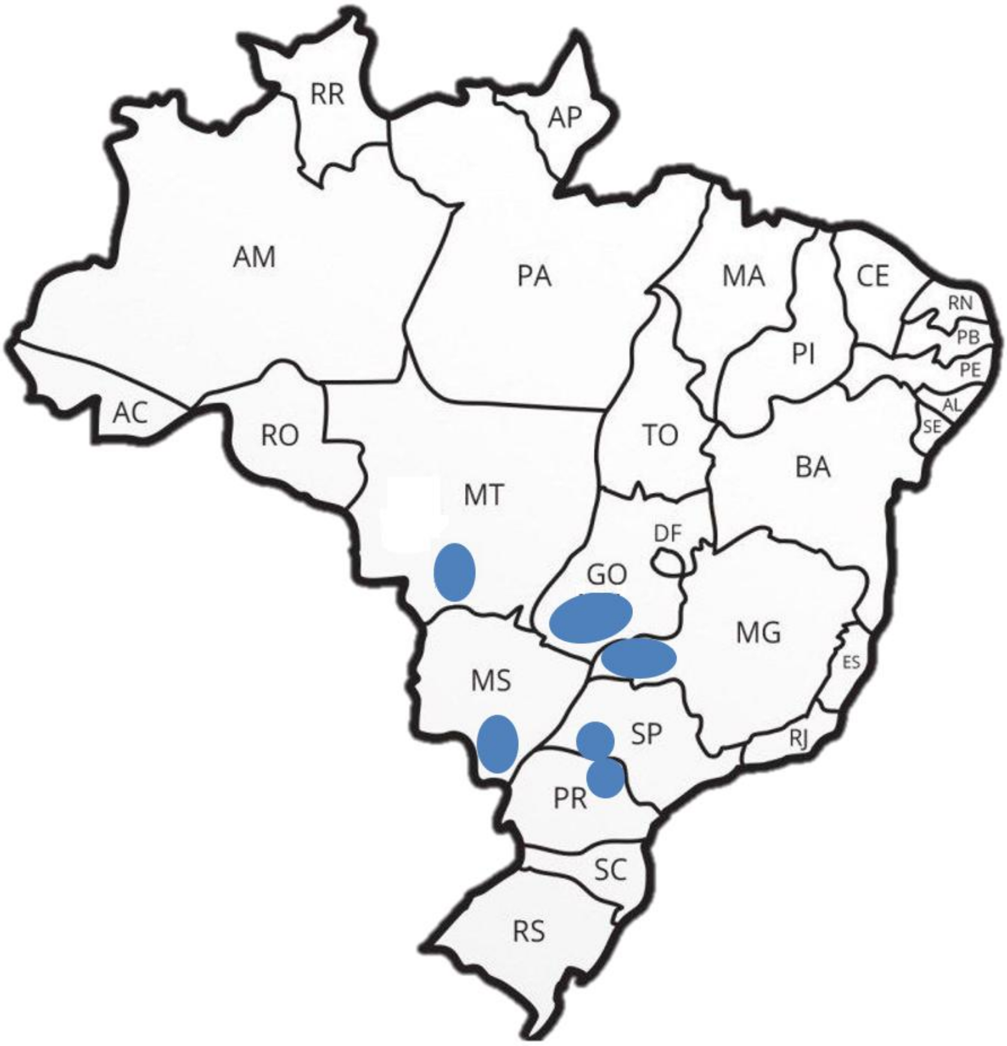

Fig. 1. Blue regions there are both the production of soybean and sugarcane, as well as the production of biodiesel and ethanol.

Risk Analysis

Table 3 describes the values found by the Hommel's diagram for methanol and ethanol, along with the meaning of each value [28]. The information in Table 3 shows that ethanol has less risk to health than methanol, this is mainly because ethanol is less toxic. Table 4 focuses on this toxicity, showing the potential health effects, the median lethal dose (LD_{50}) and the lowest published lethal dose (LD_{LO}) for methanol and ethanol [29-30]. Table 4 shows that methanol has an average LD_{50} value of 1,978 mg/kg while ethanol 7.060 mg/kg, so 3.6 times more ethanol is required than methanol to kill 50% of the rat population. As for oral LD_{LO} in humans, a methane dose of 9.8 times less than ethanol is already capable of killing a human. The lower values of LD_{50} and LD_{LO} prove that ethanol is less toxic compared to methanol.

Table 3. Hommel's diagram values for methanol and ethanol.

	Methanol	**Ethanol**
Specific hazards (white)	None	None
Health risk (blue)	3 - Short exposure may cause serious residual, temporary or permanent damage.	2 - Prolonged or persistent exposure, but not chronic, can cause temporary disability with possible residual damage.
Instability/Reactivity (yellow)	0 - Normally stable, even under conditions of exposure to fire, and is not reactive with water.	0 - Normally stable, even under conditions of exposure to fire, and is not reactive with water.
Flammability (red)	3 - Liquids and solids that can ignite under almost all ambient temperature conditions.	3 - Liquids and solids that can ignite under almost all ambient temperature conditions.

Table 4. Potential health effects, LD_{50} and LD_{LO} for methanol and ethanol.

	Methanol	Ethanol
Inhalation	Causes mild irritation to mucous membranes. It has a toxic effect on the nervous system, particularly the optic nerve. Symptoms of exposure include headache, nausea, vomiting, blindness, coma, and death.	Causes irritation to respiratory system. At high concentrations, it causes problems in the central nervous system, headache, unconsciousness and coma. May cause narcotic effects.
Ingestion	Toxic! Irritates mucous membranes. May cause intoxication and blindness. Fatal dose: 100 - 125 ml.	Causes gastric irritation, vomiting and diarrhea. May cause unconsciousness, coma and death.
Skin contact	It can leave the skin dry and brittle. If absorption occurs; symptoms similar to inhalation.	Causes dermatosis and moderate irritations.
Eye Contact	Irritating. Continued exposure may cause eye injury.	Causes severe eye irritation. It can cause conjunctivitis and corneal problems.
Chronic exposure	Impairs vision and causes enlargement of the liver. Repeated or prolonged exposure may cause skin irritation.	Continued exposure to high concentrations may cause irritation of the respiratory tract, eyes, headache, dizziness, nausea and drowsiness, and may in some cases lead to total loss of consciousness. Causes mutagenic and fetal effects.
Aggravation of pre-existing conditions	People with skin disorders, eye problems, or impaired kidney and liver function may be more susceptible to the effects of the substance.	People with skin, eye, liver, kidney, chronic breathing problems or central nervous system problems may be more susceptible to the effects of this substance.
LD_{50} (Oral in rats)	1,187-2,769 mg/Kg	7,060 mg/Kg
LD_{LO} (Oral in humans)	143 mg/Kg	1,400 mg/Kg

Methanol, in addition to being the most toxic of alcohols, has the flame invisible to the naked eye, which makes it difficult to detect and control the fire. Based on the information collected so far and, in the literature, [31], the Preliminary Hazard Analysis (APP) was constructed for methanol in Table 5, and for ethanol in Table 6.

Table 5. Preliminary Hazard Analysis (APP) for methanol.

Process	Danger	Cause	Effect	Freq.	Sev.	Risk
Reception of the raw material	Leakage of methanol; Methanol vapor leak.	Inlet valve failure; Operational error.	Health damage	C	IV	4
			Explosion		IV	4
Preparation of the catalyst	Leakage of methanol	Valve failure; Operational error; Clog level display.	Health damage	D	IV	5
			Cloud Explosion		IV	5
Transesterification reaction	Leakage of methanol; Overheating of the reactor.	Valve failure; Pump failure; Flange failure; Operational error; Mechanical impact.	Health damage	C	IV	4
			Fire jet		III	3
			Explosion		III	3
Alcohol recovery	Leakage of methanol	Pipe failure; Flange failure; Valve failure; Operational error.	Health damage	C	IV	4
			Cloud Explosion		IV	4

Table 6. Preliminary Hazard Analysis (APP) for ethanol.

Process	Danger	Cause	Effect	Freq.	Sev.	Risk
Reception of the raw material	Leakage of ethanol; Ethanol vapor leak.	Inlet valve failure; Operational error.	Health damage	C	III	3
			Explosion		IV	4
Preparation of the catalyst	Leakage of ethanol	Valve failure; Operational error;	Health damage	D	III	4

		Clog level display.	Cloud Explosion		IV	5
Transesterification reaction	Leakage of ethanol; Overheating of the reactor.	Valve failure; Pump failure; Flange failure; Operational error; Mechanical impact.	Health damage	C	III	3
			Fire jet		III	3
			Explosion		III	3
Alcohol recovery	Leakage of ethanol	Pipe failure; Flange failure; Valve failure; Operational error.	Health damage	C	III	3
			Cloud Explosion		IV	4

IV. CONCLUSION

Ethanol is a viable option for replacing methanol in the transesterification stage of biodiesel. Although the liter price of ethanol can be up to 139 % more expensive than the liter of methanol, it ends up causing only a maximum increase of 3.9% in the cost of producing biodiesel. Besides that, by the analysis of cost of three points this increase does not even reach 1.5%.

One possibility to lower the cost of producing biodiesel by the ethanolic route would be an integration between the production of biodiesel and ethanol. It would be more advantageous for this integration to take place in the sugarcane and soybean producing states, which are: Paraná (PR), São Paulo (SP), Minas Gerais (MG), Mato Grosso (MT), Mato Grosso do Sul (MS) and Goiás (GO).

In addition to that, ethanol is safer than methanol both because it is much less toxic, and because it is easy to identify the focus of fire, since methanol has an invisible flame. Only with the use of ethanol can biodiesel be considered a biofuel, with all its raw materials coming from renewable sources.

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