Renewable and Non-Renewable Exergy Costs and CO_2 Emissions in the Production of Fuels for Brazilian Transportation Sector

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Abstract:

An exergy and environmental comparison between the fuel production routes for Brazilian transportation sector, including fossil fuels (natural gas, oil-derived products and hydrogen), biofuels (ethanol and biodiesel) and electricity is performed, and the percentage distribution of exergy destruction in the different units of the processing plants is characterized. An exergoeconomy methodology is developed and applied to properly allocate the renewable and non-renewable exergy costs and CO2 emission cost among the different products of multiproduct plants. Since Brazilian electricity is consumed in the upstream processing stages of the fuels used in the generation thereof, an iterative calculation is used. The electricity mix comprises thermal (coal, natural gas and oil-fired), nuclear, wind and hydroelectric power plants, as well as bagasse-fired mills, which, besides exporting surplus electricity, also produce sugar and bioethanol. Oil and natural gas-derived fuels production and biodiesel fatty acid methyl-esters (FAME) derived from palm oil are also analyzed. It was found that in spite of the highest total unit exergy costs correspond to the production of biofuels and electricity, the ratio between the renewable to non-renewable invested exergy (cR/cNR) for those fuels is 2.69 for biodiesel, 4.39 for electricity, and 15.96 for ethanol, whereas for fossil fuels is almost negligible.

Keywords:

Renewable, Non-renewable, Exergy Cost, Transportation Sector, CO_2 Emissions.

1. Introduction

At a time of economic uncertainty and environmental concerns, one of the major consumers of the world's primary energy, namely the transportation sector, is recognized as a hugely important issue across the global economy [1]. In fact, the rational use of the most suitable fuels favorably affects the way scarce resources are used, improving the economy performance and reducing the environmental impact. However, the quest for higher energy efficiencies through the advent of new technologies may also alter the vehicle demand profiles, as well as modify the levels of emissions and fuel consumption. Thus, gradual improvements on technology and regulatory policies must be incorporated only after a detailed performance and sustainability assessment has been achieved, including not merely the end use stages, but also the upstream fuel production processes [2]. Because their non-renewable nature, increasing price and the effects of global warming, the fossil fuels dependence of global transportation sector (94%) is forecast to decline to 89% by 2030 [3], as vehicles running on renewable sources gain more attention and engines based on such fuels undergone constant developments. However, the extent to which fossil fuel substitution can be achieved largely depends on how renewables are produced, which is likely to stay uneconomic in most markets where continued cost reductions are still required as renewable fuels scale up [3,4]. On the other hand, most regions do not generate enough low CO_2 electricity to enable electric vehicles (EV) and plug-in hybrid EV (PHEV) to contribute significantly to large CO_2 reductions. Consequently, in the absence of strong efforts to decarbonize electricity generation, vehicle electrification also seems unlikely to be an environmentally friendly and cost-effective route [1]. Fortunately, both Brazilian electricity and transportation sector mixes have been characterized by an approach that is peculiar within the international context of dependence on fossil fuels. Brazilian electricity mix is mainly dominated by renewable energy sources (89%) and although diesel oil (48.6%), gasoline (28.2%) and natural gas (2.2%) still dominate the transportation sector mix, sugar-cane ethanol shares more than 14.5% [5,6], and it is expected to achieve 30% in 2030 [7]. Transportation sector in Brazil consumed almost 30% of national energy demand and produced 48% of the total CO_2 emissions through four types of vehicles technologies: gasoline C-dedicated, flex-fuel, hydrated ethanol-dedicated (commercialized until 2007), compressed natural gas (CNG) and diesel B05 (5% in vol. biodiesel), the latter used only by commercial and passenger light vehicles with a minimum capacity load of 1000kg [8,9,10]. Moreover, other technologies such as test fleets of electric taxi cabs earned recent interest and started to be commercialized. In this way, a rational comparison of the fuel options for the Brazilian scenario is required, encompassing petroleum and natural gas derivatives, biofuels, as well as electricity. This provides an opportunity to quantify the renewable and non-renewable exergy consumption and thereby pursues and prioritizes the use of the most environmentally friendly sources of energy, also serving as a theoretical base for issuing guidelines in the transportation sector. Some studies based on Extended Life Cycle Analysis (ELCA) have addressed specific assessments on biofuels or petroleum derivatives production routes. Beer *et al.* [11] in Australia, and Hossain *et al.* [12] in Bangladesh, performed a life cycle analysis of the production routes of vehicle fuels including fossil and alternative sources. In Brazil, D'Agosto and Ribeiro [13] performed a Life Cycle Inventory (LCI) to determine the total and renewable energy and greenhouse gas emissions of gasoline, CNG and ethanol-powered vehicles in the case of Rio de Janeiro. The authors concluded gasoline C presents the lowest energy consumption along its life cycle. Hawkins *et al.* [14] performed an environmental life cycle assessment of conventional and electric vehicles, concluding that electric vehicles powered by the present European electricity mix offer a 10% to 24% decrease in global warming potential (GWP) relative to conventional diesel or gasoline vehicles. Ma *et al.* [15] carried out a comparison between the lifecycle greenhouse gas (GHG) emissions of battery electric vehicles in Europe, identifying the need to correctly assign the relevant GHG emissions to the electricity consumed in battery-powered vehicles, i.e. the emissions associated to the well to tank analysis. Seckin *et al.* [16] developed the analysis of transportation sector in Turkey, by using the Extended Exergy Accounting (EEA), obtaining global exergy efficiency as low as 36%, mainly due to the high proportion of non-renewable energy sources used in the transportation mix. However, these works are all based on the principle of the First Law of Thermodynamics (except for [16]), which does not take into account the *quality* of the energy consumed and the exergy destruction (entropy generation) through the irreversible processes occurring in the fuel production routes. Thus, in this work an exergy and environmental analysis based on the Second Law of Thermodynamics is presented, encompassing the integrated production routes of the conventional and alternative fuels of the Brazilian transportation mix and accounting for their CO_2 emission costs.

2. Methodology

The approach used in this analysis is based on thermoeconomy methodologies [17-23] and aims to properly allocate the renewable and non-renewable exergy costs and CO_2 emission costs along the different production routes. Each fuel production route is composed of three different types of stages, namely *supply stage*, *transformation stage* and *end use stage*, used to represent each process that the different fuels are subjected to along the entire production and end use route, as shown in Figure 1. The Non-Renewable Unit Exergy Cost (c_{NR}) is defined as the quantity of non-renewable exergy necessary to produce one unit of exergy of analyzed substance/flow (e.g., water, wind, biomass, nuclear or fossil fuel) or electricity [kJ/kJ]. Thus, the Total Unit Exergy Cost (c_T) includes the Renewable (c_R) and Non-Renewable (c_{NR}) Unit Exergy Costs. Analogously, the CO_2 emissions cost (c_{CO2}) is defined as the amount of total CO_2 emitted (directly and indirectly) to obtain one unit of exergy of analyzed substance/flow or electricity [gCO_2/kJ]. It must be pointed out that, even though the term "fuel" is generally used to designate substances that store chemical exergy, in contrast to those used to produce mechanical exergy from their kinetic or potential exergy (such as wind or water in a reservoir), the term “fuel” in this paper also represents any substance used to produce electricity or mechanical power (such as wind in wind farms and nuclear fuel in pressurized water reactors).

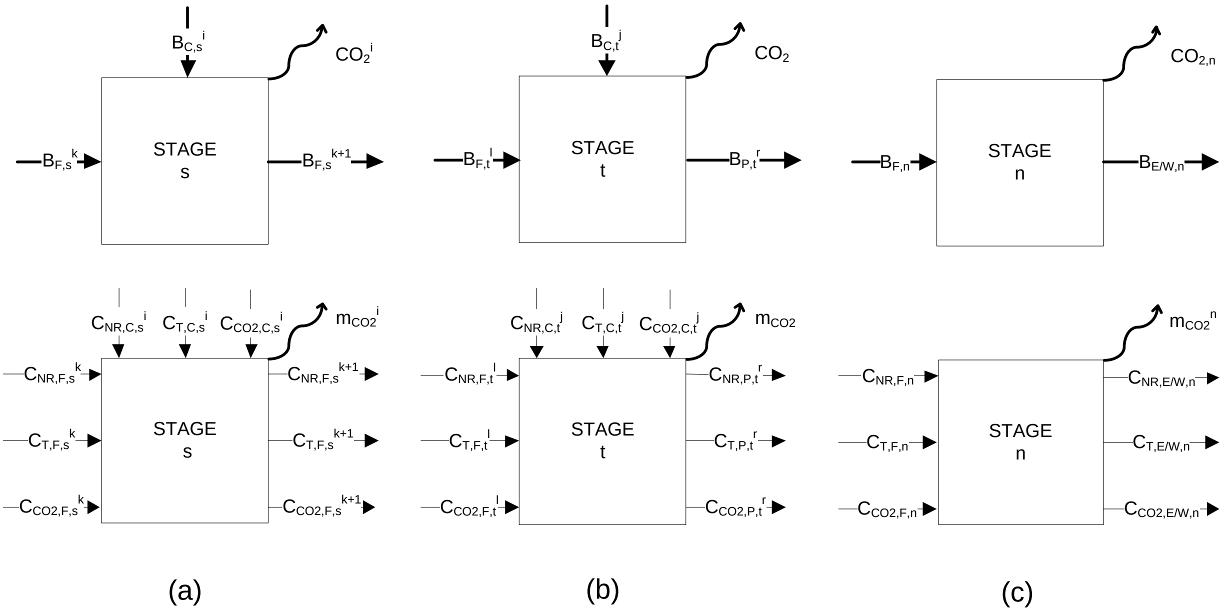

Fig. 1. Exergy and CO_2 emissions costs accumulation stages: (a) Supply stage (s); (b)Transformation stage (t); (c) End Use stage (n).

2.1. Supply stage

At the first stage (k=0) of the so-called *supply stages* [1] (*s*), the exergy of the fuel ($B_{F,s}^{0}$) as present in the environment (petroleum and gas from well, coal and uranium ore, biomass, wind and water) enters the control volume used to analyze each route. As the stream passes through the downstream *supply stages* (k > 0), the total and non-renewable exergy costs as well as CO_2 emission cost related to the *supplied* stream, $B_{F,s}^{k}$, are accumulated along the route. Since the exergy consumed in the *supply stages*, $B_{C,s}^{i}$, has also been previously processed, either in the same stage (self-consumption of supplied fuel) or in another stage (e.g. a petroleum refinery product), it also carries total and non-renewable exergy costs and CO_2 emission cost, besides producing direct CO_2 emissions when consumed in the respective *supply stage*. In this way, the scheme that better fits the *supply stage* is presented in Fig 1.a, where *k* and *k+1* stand for the supplied fuel streams (*F*) that enter and leave the analyzed stage (*s*) and *i* represent the different exergy consumptions (*C*) of the same stage. Processes that can be considered *supply stages* are extraction, mining, agriculture, transportation of pre-processed fuel or feedstock, and fuels distribution processes. Furthermore, since exergy consumption in construction, operation and decommissioning stages can be amortized along the lifetime of the equipment or plant, then, those stages can also be considered as *supply stages*. Accordingly, the inputs of the *supply stage* correspond to the exergy of the supplied fuel (F) and the exergy consumed (*C*) in that stage. Meanwhile, outputs correspond to the exergy of the supplied fuel leaving the *supply stage* and the CO_2 emissions related to such stage. Because these stages ‘supply’ the raw material, feedstock and fuels (pre-processed or finished) necessary to *transformation* and *end use stages* to operate, a hypothesis that simplifies the analysis of this kind of stages can be

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[1] Stages whose objective is the extraction, transportation and preparation of feedstock or supplied fuels, *F*, used in the transformation and end use stages. These stages require additional exergy inputs called exergy consumption, *C*, besides of that supplied by the fuel *F* itself.

considered. By regarding the exergy of the fuel supplied to the *transformation*, $B^{l}_{F,t}$, or *end use stage*, $B^{i}_{F,n}$, as the basis to calculate the unit exergy and CO2 emission costs of the streams that go through the upstream *supply stages* along the different fuel production and electricity generation routes, consequently: $B^{0}_{F,s} = ... = B^{k}_{F,s} = B^{k+1}_{F,s} = ... = B_{F,\{t\ or\ n\}}$. In this way, an analysis based on exergy cost balances instead of exergy rate/flow rate balances is carried out and the irreversibility, i.e., the exergy destruction of each supply stage, B^{i}_{gen}, does not need to be explicitly known. It is pointed out that this hypothesis does not necessarily imply that exergy consumed (C) on each stage is totally destroyed, but that the exergy cost of the fuel that lastly attains the *transformation* and *end use stages* is burdened with the global effect of the irreversibilities present along all the preceding *supply stages*. Hence, the mathematical representation of the total and non-renewable exergy cost accumulation for a given *supply stage* (see Fig 1.a) can be expressed as in (1) and (2), respectively, where B stands for the exergy rate/flow rate of the analyzed stream [kW]:

$$c^{k+1}_{T,F,s} B^{k+1}_{T,F,s} = c^{k}_{T,F,s} B^{k}_{T,F,s} + \sum_{i} c^{i}_{T,C,s} B^{i}_{T,C,s} \tag{1}$$

$$c^{k+1}_{NR,F,s} B^{k+1}_{T,F,s} = c^{k}_{NR,F,s} B^{k}_{T,F,s} + \sum_{i} c^{i}_{NR,C,s} B^{i}_{NR,C,s} \tag{2}$$

Analogously, the CO2 emission cost balance can be written as in (3), where direct CO2 emissions[2], related to the consumption of exergy input *i* in each stage, are accounted for in the M^{i}_{CO2} term [gCO2/s], analogous to *Z* term used to account for capital investment in thermoeconomy:

$$c^{k+1}_{CO_2,F,s} B^{k+1}_{T,F,s} = c^{k}_{CO_2,F,s} B^{k}_{T,F,s} + \sum_{i} \left(c^{i}_{CO_2,C,s} B^{i}_{T,C,s} + M^{i}_{CO_2,s} \right) \tag{3}$$

Then, by considering that $B^{0}_{F,s} = ... = B^{k}_{F,s} = B^{k+1}_{F,s} = \ldots = B_{F,\{t\ or\ n\}}$, when dividing both sides of (1-3) by the exergy of the fuel that goes through the analysed *supply stage* (*s*) ($B^{k+1}_{F,s}$), those equations can be simplified to (4-6):

$$c^{k+1}_{T,F,s} = c^{k}_{T,F,s} + \sum_{i} \left(c^{i}_{T,C,s} \cdot r^{i}_{T,s} \right) \tag{4}$$

$$c^{k+1}_{NR,F,s} = c^{k}_{NR,F,s} + \sum_{i} \left(c^{i}_{NR,C,s} \cdot r^{i}_{NR,s} \right) \tag{5}$$

$$c^{k+1}_{CO_2,F,s} = c^{k}_{CO_2,F,s} + \sum_{i} \left(c^{i}_{CO_2,C,s} \cdot r^{i}_{T,s} + m^{i}_{CO_2,s} \right) \tag{6}$$

where $r^{i}_{T,s}$ and $r^{i}_{NR,s}$ represent the *i-th* total and non-renewable exergy consumption per unit of exergy of supplied fuel [kJ/kJ] , respectively, and $m^{i}_{CO_2,s}$ is the amount of CO2 directly emitted owed to the burning of the *i-th* consumed fuel per unit of exergy of supplied fuel [gCO2/kJ]. Those terms can be calculated using (7-9):

$$r^{i}_{T,s} = \frac{B^{i}_{T,C,s}}{B^{k+1}_{T,F,s}} \quad (7) \qquad r^{i}_{NR,s} = \frac{B^{i}_{NR,C,s}}{B^{k+1}_{T,F,s}} \quad (8) \qquad m^{i}_{CO_2,s} = \frac{M^{i}_{CO_2,s}}{B^{k+1}_{T,F,s}} \quad (9)$$

2.2. Transformation stage

The objective of *transformation stages* (Fig. 1.b) is the processing and transformation of raw materials, feedstock and pre-processed fuels, supplied by *supply stages*, in order to produce value-added products (e.g. vehicle fuels) and other co-products used in other stages. When more than one product is produced in the same stage, a detailed exergoeconomy analysis of the specific stage must be employed to properly split the exergy and CO2 emission costs among all the different products in

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[2] Net or fossil CO2 emissions which increase the amount of CO2 present in the atmosphere.

a rational manner. This approach avoids classifying the products between main products and by-products, splitting the costs between all the products of the same plant based in the amount of the embodied exergy. An exergy cost balance for a given *transformation stage*, based on the *black box* analysis shown in Fig. 1.b, yields to coarse results and a better accuracy can be obtained if a more detailed analysis is achieved. Fig. 2 evidences that a *transformation stage* can be analyzed as being composed of a series of sub-stages, which, in turn, may be considered as *supply stages* (sub-stage t4, e.g. as sugar cane washing and transportation units in the mill, water cooling unit and so forth) or *transformation stages* (sub-stage t1 and t2, e.g. as fermentation processes, fluidized catalytic cracking unit, et cetera.), as well as *end use stages*, which will be analyzed later (sub-stage 5, e.g. as generation of electricity exported to the grid).

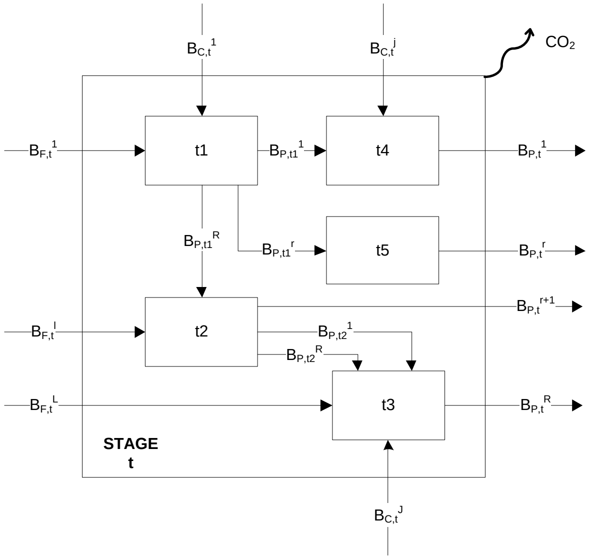

Figure 2. Detailed analysis of a transformation stage.

Thus, based on the control volume adopted for the different sub-stages, the total and non-renewable exergy costs and CO_2 emission cost balances for each *sub-stage* (t1, t2, t3…) composing the *transformation stage*, can be written as in (10-11)

$$\sum_{r} c_{T,P,t}^{r} B_{T,P,t}^{r} = \sum_{l} c_{T,F,t}^{l} B_{T,F,t}^{l} + \sum_{j} c_{T,C,t}^{j} B_{T,C,t}^{j} \tag{10}$$

$$\sum_{r} c_{NR,P,t}^{r} B_{T,P,t}^{r} = \sum_{l} c_{NR,F,t}^{l} B_{T,F,t}^{l} + \sum_{j} c_{NR,C,t}^{j} B_{NR,C,t}^{j} \tag{11}$$

where *B* stands for the exergy rate/flow rate of the supplied fuels (*l*) and the exergy consumptions (*j*) entering the *transformation stage*, as well as for the exergy rate/flow rate of the different products (*r*) of the respective stage. On the other hand, the CO_2 emission cost balances can be written as in (12), where the direct CO_2 emissions either produced by burning the different fuel consumptions (*j*), or as a result of the chemical reactions arisen from the transformation processes of the supplied fuels (e.g. fermentation, steam reforming process, etc.), are accounted for in the $M_{CO_2,t}^{j}$ and the $M_{CO_2,reac}$ terms [gCO2/s], respectively:

$$\sum_{r} c_{CO_2,P,t}^{r} B_{T,P,t}^{r} = \sum_{l} c_{CO_2,F,t}^{l} B_{T,F,t}^{l} + \sum_{j} \left(c_{CO_2,C,t}^{j} B_{T,C,t}^{j} + M_{CO_2,t}^{j} \right) + M_{CO_2,reac} \tag{12}$$

2.3. End use stage

In the *end use stages* (Fig. 1.c) it is considered that the only exergy input is the *supplied fuel*, $B_{F,n}^{i}$, used to generate electricity (i.e. power plant) or mechanical power (e.g. a vehicle, in the case of transportation sector) ($B_{E/W,n}$). Thus, in this kind of stage no additional exergy inputs, aside from the fuel delivered from *supply stages* or *transformation stages*, are considered. Hence, the supplied fuel is responsible for the direct CO_2 emissions, provided that it contains fossil carbon (Fig. 1.c). In this way, in the case of the *end use stage* the terms $B^i_{T,C,n}$ and $B^i_{NR,C,n}$ are null by definition, so the balance for exergy costs and CO_2 emission cost can be written as shown in (13-15):

$$c_{T,E/W,n}\, B_{E/W,n} = c_{T,F,n}\, B_{T,F,n} \tag{13}$$

$$c_{NR,E/W,n}\, B_{E/W,n} = c_{NR,F,n}\, B_{T,F,n} \tag{14}$$

$$c_{CO_2,E/W,n}\, B_{E/W,n} = c_{CO_2,F,n}\, B_{T,F,n} + M_{CO_2,n} \tag{15}$$

By dividing both sides of (13-15) by the electricity generated or the mechanical power produced in the respective stage ($B_{E/W,n}$), then (16-18) are obtained:

$$c_{T,E/W,n} = c_{T,F,n}\, r_{T,n} \tag{16}$$

$$c_{NR,E/W,n} = c_{NR,F,n}\, r_{NR,n} \tag{17}$$

$$c_{CO_2,E/W,n} = c_{CO_2,F,n}\; r_{T,n} + m_{CO_2,n} \tag{18}$$

where $r_{T,n}$ represents the total exergy consumption per unit of electricity generated or mechanical power produced [kJ/kJ], and $m_{CO_2,n}$ the amount of CO_2 directly emitted in the *end use stage* per unit of electricity generated or mechanical power produced [gCO_2/kJ]. Those terms can be calculated by using (19-20):

$$r_{T,n} = \frac{B_{T,F,n}}{B_{E/W,n}} \tag{19}$$

$$r_{CO_2,n} = \frac{M_{CO_2,n}}{B_{E/W,n}} \tag{20}$$

By inspection, the values of $r_{T,n}$ and $m_{CO_2,n}$ correspond to the inverse of the exergy efficiency, η_{ex}, and the specific direct CO_2 emissions (if present) at the *end use stage*, respectively. It is worth to notice that, whereas the exergy efficiency of the electricity generation plants can be considered as reported in literature for different technologies [23], in the case of the *end use* of a vehicle fuel used in transportation sector (or other fuels used in residential or industrial sectors), the definition of exergy efficiency will depend on the “useful product” of the *end use stage* (transport service, heating, cooling, lighting) as discussed in [24]. In Fig. 3, a simplified representation of the relationships between the different types of stages is shown. The supply stages s = 1, 2 and s = 3, 4 could be interpreted as extraction and transportation stages for crude oil and non-associated natural gas, respectively, to refinery (*transformation sub-stages* called t1 and t2). Meanwhile, stages s = 5, 6 and 7 could be understood as extraction, transportation and stock of mineral coal. The end use stages n = 1 and n = 2 may be interpreted as an oil-fired thermoelectric power plant and a vehicle running on, say, diesel oil. Other products of the transformation stage t = 1 are not used either in transportation sector applications nor electricity generation; nevertheless, this analysis still can be used to allocate their corresponding unit exergy and CO_2 costs (e.g. coke, sulfur in petroleum refineries, or glycerol, surplus bagasse, and so forth, in biorefineries).

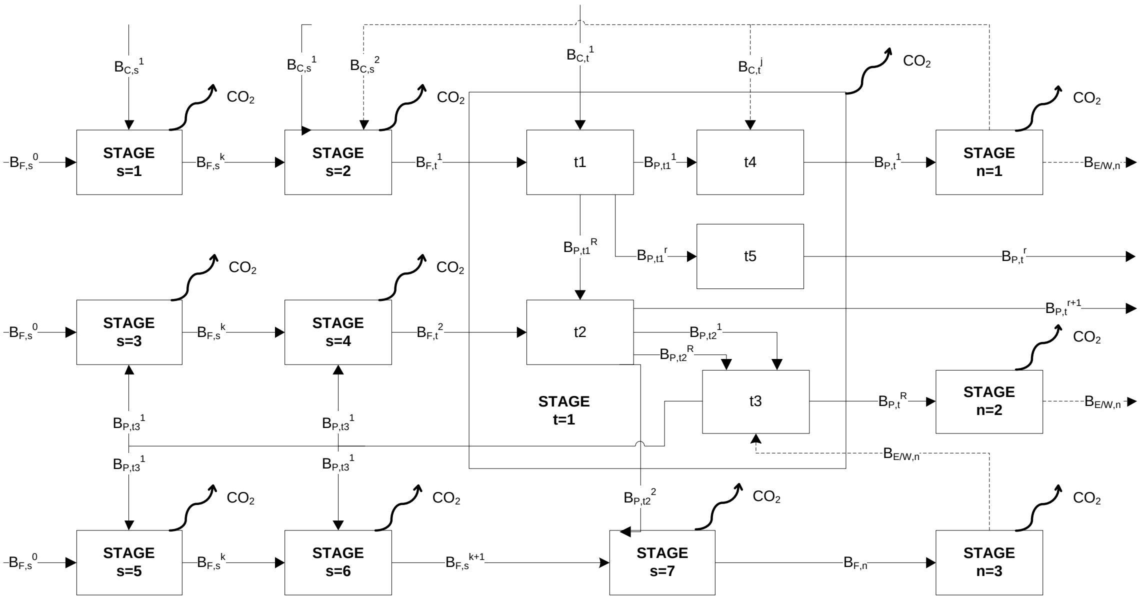

Fig. 3. Relationship between the different types of stages and sub-stages

The calculation procedure of the exergy consumption in the different stages along the electricity generation routes in Brazilian electricity mix follows closely that carried out by [23]. It is important to notice that, often in Life Cycle Analysis (LCA) literature, the energy consumption (“thermal” or electrical) in each stage of a given electricity generation route is reported in the way of consumed energy per unit of electricity generated (or *I/O*, input-output ratio, in kJ/kWh or GW/GW$_e$). Based on those values, it is possible to calculate the exergy consumption per unit of exergy of a supplied fuel (the fuel that goes through the *supply stage*), quantity that was previously defined as $r_s^{\,i}$ [kJ/kJ]. This is achieved by using the energy efficiency of the electricity generation stage, η_{en}, and the value of φ, i.e., the ratio between the specific chemical exergy (b^{CH}) and the lower heating value of the fuel (LHV) [25], for both consumed (φ_{C}^{i}) and supplied fuel (φ_{F}^{n}), according to (21):

$$r_s^{\,i} = \underbrace{\left(\frac{\mathrm{E}^{i}_{\mathrm{C,s}}}{\mathrm{E}_{\mathrm{E/W,n}}}\right)}_{I/O} \cdot \varphi^{i}_{\mathrm{C,s}} \cdot \underbrace{\left(\frac{\mathrm{E}_{\mathrm{E/W,n}}}{\mathrm{E}_{\mathrm{F,n}}}\right)}_{\eta_{en}} \cdot \frac{1}{\varphi_{\mathrm{F,n}}} \tag{21}$$

Here $\mathrm{E}^{i}_{\mathrm{C,s}}$ stands for energy rate/flow rate of the consumed fuel, which, in turn, can be total or non-renewable, and $\mathrm{E}_{\mathrm{F,n}}$ is the energy of the supplied fuel. Besides, $\mathrm{E}_{\mathrm{E/W,n}}$ is the electricity generated on each route. It must be pointed out that in the case of the exergy associated to substances like water and wind, as well as to electricity, the value of φ is considered equal to unity, since the potential and kinetic energies as well as the electric energy are equal to the potential, kinetic or electric exergies of the substances or electricity, respectively. In the case of the power plant, the value of $r_n = 1/\eta_{ex}$ can be calculated by using (22):

$$r_n = \underbrace{\left(\frac{\mathrm{E}_{F,n}}{\mathrm{E}_{\mathrm{E/W,n}}}\right)}_{1/\eta_{en}} \cdot \varphi_{\mathrm{F},n} \tag{22}$$

Meanwhile, direct CO_2 emissions, derived from the combustion of a fuel containing carbon, will depend on the amount of consumed fuel and its fossil carbon content[3]. Those emissions can be calculated according to (23):

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[3] Biomass-derived net CO_2 emissions are considered null, since the CO_2 emitted by those sources undergoes a closed cycle of absorption and release by the plants [26].

$$M_{CO_2} = M_C \cdot I_C \cdot R_m \tag{23}$$

where R_m ~ 3.7 [kg_{CO2}/kg_{Carbon}] is the ratio between the molecular weight of carbon dioxide and atomic carbon, M_C [kg_{Fuel}/s] is the fuel consumption rate, and I_C [kg_{Carbon}/ kg_{Fuel}] is the fossil fuel carbon content of the consumed fuel, based on the elemental analysis. In this way, the net direct CO_2 emissions per unit of exergy of fuel passing through the *supply stage* (s) [gCO_2/kJ] can be calculated according to (24):

$$m^i_{CO_2,s} = \underbrace{\left(\frac{E^i_{C,s}}{E_{E/W}}\right)}_{I/O} \cdot \underbrace{\left(\frac{E_{E/W}}{E_{F,n}}\right)}_{\eta_{en}} \cdot \underbrace{\left(\frac{M^i_{C,s}}{E^i_{C,s}}\right)}_{1/LHV^i_C} \cdot I^i_{C,C,s} \cdot R_m \cdot \frac{1}{\varphi_{F,n}} \cdot 1000 \tag{24}$$

where $I^i_{C,C,s}$ represents the fossil carbon content of the *i-th* fuel consumed in the *supply stage (s)*, which clearly is zero in the case of the electricity consumption. Analogously, in order to determine the direct CO_2 emissions per unit of electricity generated in the *electricity generation stage (n)*, those values can be calculated by using (25) [gCO_2/kJ]:

$$m_{CO_2,n} = \underbrace{\left(\frac{E_{F,n}}{E_{E/W,n}}\right)}_{1/\eta_{en}} \cdot \underbrace{\left(\frac{M_{C,s}}{E_{F,n}}\right)}_{1/LHV_C} \cdot I_{C,F,n} \cdot R_m \cdot 1000 \tag{25}$$

where $I_{C,F,n}$ represents the carbon content of the fuel fed to the *end use stage* (namely, the power plant). By definition, $I_{C,F,n}$ is zero for the "fuels" of wind farms, nuclear power plants and hydropower plants. Finally, it is emphasized that, differently from unit exergy cost balances, for which the initial value of unit exergy costs entering the control volume of each route can be regarded as the unity (or a given value if known from other exergoeconomy analysis), the initial value for CO_2 emission cost balances is considered null. Moreover, since some processed streams are consumed in other stages, and some stages consume electricity from the grid, an iterative calculation is employed to solve the set of non-linear equations for the mass, exergy, unit exergy costs and CO_2 emission cost of the fuels involved in the Brazilian transportation sector.

3. Petroleum and natural gas production route

Figure 4 shows the stages of the routes of production of natural gas and petroleum-derived fuels. This scheme is used to calculate the accumulated unit exergy cost and CO_2 emission cost according to the methodology proposed in section 2. The streams are labeled by using a letter based on the previous stage, i.e. crude oil or natural gas followed by "ES" represents the stream leaving the extraction and primary separation process. Analogously, "T" and "P" stand for the streams leaving the shuttle tanker and the pipeline transportation stage, respectively. Since almost 90% of Brazilian petroleum production is offshore, the petroleum is considered as extracted from the well of an offshore platform [27]. According to Nakashima et al. [28], the non-renewable unit exergy costs for crude oil and natural gas after extraction and primary separation are 1.006kJ/kJ and 1.025kJ/kJ, respectively. Since part of the produced natural gas is consumed in this stage, the exergy consumption and CO_2 emissions per unit of exergy of crude oil and natural gas produced can be obtained. In this way, CO_2 emission costs can also be easily calculated and those values are shown in Table 1.

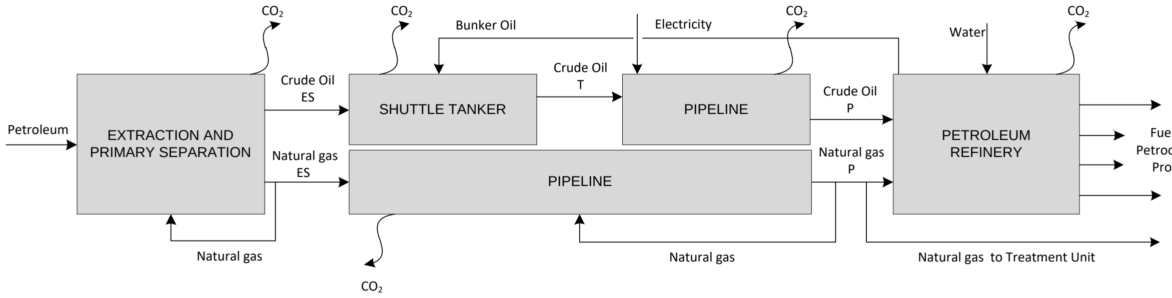

Fig. 4. Production route of petroleum-derived fuels.

The exergy consumption in oil transportation from sea to land is calculated assuming the use of a shuttle tanker Suezmax-type. By considering a travelling route of 800 km at a speed of 13 knots and a load capacity of 155,000 tons, as well as the offloading operations of platform and tanker, it is possible to calculate the exergy consumption of bunker fuel and the direct CO_2 emissions as 42.32 $kJ/(km.t_{Oil})$ and 3.06 $gCO_2/(km.t_{Oil})$ [27]. As bunker fuel is a processed fuel, the determination of its unit exergy costs and CO_2 emission cost requires an iterative calculation. The oil transportation from land base to the refinery is performed through pipelines by consuming electricity from the national electric grid. Thus, by using the Colebrook-White correlation [29] for pressure drop calculation, in addition to data of petroleum pipeline and a pumping efficiency of 60%, the calculated exergy consumption is 100.3$kJ/(km.t_{Oil})$. Since electricity consumed in land oil transportation comes from the national grid, the unit exergy costs and CO_2 emissions of transported oil will depend on the whole electricity mix. In the case of natural gas transportation through pipelines, it is considered that part of transported gas is burnt in gas turbines to drive the gas compressors. By considering a transportation length of 1350 km through the Brazil-Bolivia gas pipeline (GASBOL) [30], together with an isentropic compression efficiency of 80% and a gas turbine efficiency of 37% (LHV basis), it is possible to determine the exergy consumption and CO_2 emissions related to natural gas transportation as 1.063 $kJ/(km.t_{NG})$ and 58.2 $gCO_2/(km.t_{NG})$, respectively. Natural gas composition reported by [31] is used to calculate the φ value for natural gas. Table 1 presents the unit exergy cost and CO_2 emission of the different streams along the production route of the petroleum-derived fuels and natural gas. These values are used as input data in exergoeconomy analysis for the refinery stage.

Table 1. Unit exergy cost and CO_2 emission cost of the different streams along the production route of petroleum-derived fuels and natural gas.

Stream	c_T **(kJ/kJ)**	c_R **(kJ/kJ)**	c_{NR} **(kJ/kJ)**	c_{CO2} **(gCO_2/kJ)**
Petroleum	1.0000	0.0000	1.0000	0.0000
Crude oil - ES	1.0060	0.0000	1.0060	0.0006
Natural gas - ES	1.0250	0.0000	1.0250	0.0006
Bunker fuel	1.0504	0.0008	1.0496	0.0029
Crude oil – T	1.0073	0.0000	1.0073	0.0007
Electricity	1.7956	1.4628	0.3328	0.0174
Water	1.0000	1.0000	0.0000	0.0000
Crude Oil – P	1.0082	0.0007	1.0075	0.0007
Natural gas – P	1.0550	0.0000	1.0550	0.0023

Refining stage is based on a typical petroleum refinery as studied by Silva and Oliveira Jr. [32] and Silva et al. [27], with a cracking-coking scheme (See Appendix A.1). A specific exergoeconomy analysis encompassing the different production units of the petroleum refinery is used to calculate the exergy and CO_2 emission costs for the different products, including diesel and fuel oil used in other stages and for power generation. In Fig. 5 the percentage distribution of destroyed exergy at different units in the refinery is presented.

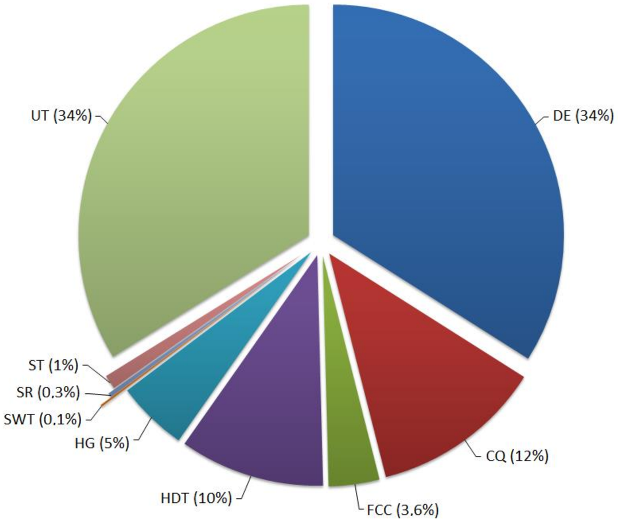

Fig.5. Percentage distribution of destroyed exergy at different units in the petroleum refinery. DE, combined distillation unit; CQ, delayed coking unit; FCC, fluidized catalytic cracking unit; HDT, hydrotreating unit; HG: hydrogen generation unit; SR: sulfur recovery unit; ST: storage and transfer unit; SWT: sour water treatment unit; UT: utilities plant.

As it can be seen in Fig. 5, utilities plant is responsible for 34% of the destroyed exergy, due to the highly irreversible processes that occur in that unit such as steam throttling for pressure reduction, fossil fuel combustion and heat exchanges with finite temperature differences. Combined distillation process is responsible for one-third of the exergy destruction in the refinery owed to the presence of highly irreversible combustion reactions present at the burning of the fuel consumption source used to distillate the mixture. Meanwhile, sulfur recovery, storage and transfer, and acid water treatment units together are responsible for only 1.4% of the exergy destruction. The renewable and non-renewable unit exergy costs for the different products of the refinery are summarized in Table 2:

Table 2. Renewable and non-renewable unit exergy costs and CO_2 emission cost for the different products of the petroleum refinery.

Product	**c_T (kJ/kJ)**	**c_R (kJ/kJ)**	**c_{NR} (kJ/kJ)**	**c_{CO2} (gCO_2/kJ)**	**c_R/c_{NR}**
GLP	1.0738	0.0010	1.0728	0.0081	0.0009
Kerosene	1.0308	0.0010	1.0298	0.0016	0.0010
Gasoline	1.0810	0.0011	1.0799	0.0103	0.0010
Diesel	1.0308	0.0010	1.0298	0.0016	0.0010
Naphtha	1.0400	0.0011	1.0389	0.0021	0.0011
Gasoil	1.0422	0.0010	1.0412	0.0028	0.0010
Sulphur	1.0928	0.0011	1.0917	0.0075	0.0010
Coke	1.0726	0.0011	1.0715	0.0037	0.0010
Diesel HDT	1.1129	0.0010	1.1119	0.0074	0.0009
Hydrogen	1.5139	0.0002	1.5137	0.0739	0.0013

According to Table 2, specific CO_2 emissions associated with gasoline and diesel oil production amount to 0.0103 and 0.0016gCO_2/kJ_{fuel}, respectively. Considering the chemical exergy and density of those produced fuels, these values are equivalent to 328.25$kgCO_2/m^3$ for gasoline and 63.13$kgCO_2/m^3$ for diesel oil. This is a consequence of a further processing of gasoline compared to common straight run diesel. On the other hand, because of the high energy intensity of the endothermic steam methane reforming (SMR) process and large CO_2 emissions in reforming and shift reactions of hydrogen generation, this fuel presents the largest CO_2 emission cost and its unit exergy costs are greater than any other petroleum-derived fuel, even than that of hydro-treated diesel oil. Although hydrogen could achieve a high efficiency conversion through water electrolysis (70%), this process remains a cost-intensive process due the massive use of electricity, and the economic attractiveness depends significantly on the relative costs for hydrogen and natural gas. At present, the capital investments of hydrogen production are about five times smaller via natural gas rather than wind or solar energy in Brazil [33]. As a consequence, the share of hydrogen production by means of SMR process is substantially higher than for other technologies [34], so that, in this work such scenario is adopted. Moreover, it must be noticed that c_R/c_{NR} ~ 0.0010 for the different products of the refinery. The reason is that, along the production route of petroleum-derived fuels, the only renewable exergy contribution comes from the electricity used in the transportation of crude oil via pipelines. All the remaining exergy sources consumed are basically non-renewable. Finally, for natural gas dehydration and treatment process data, the energy consumption reported for Cabiúnas Treatment Plant (TECAB), with a processing capacity of 575,000 m^3 of natural gas, is considered. According to [35], in order to treat 467,509kJ of natural gas, 8397kJ of natural gas and 1901kJ of electricity are required. Thus, by using this data and φ value for natural gas, an exergy consumption of 0.0180kJ of natural gas and 0.0039kJ of electricity per kJ of processed natural gas is calculated. Hence, the renewable and non-renewable exergy costs and CO_2 emission cost of treated natural gas are obtained as 0.0189kJ/kJ, 1.0978kJ/kJ and 0.0049gCO_2/kJ, respectively.

4. Biodiesel production route

Around the world, different cultures, including soy, sunflower, rapeseed, palm fruit, coconut or even wasted frying oil from animal fats are used to produce biodiesel. However, oil-seed crops other than tropical palm oil (with 18-26% oil and producing 5900 L/ha) yield fairly small amounts of fuel per hectare, which impacts negatively the production of food supplies and increases the fossil energy expended in agriculture and transport activities. This fact has suggested the culture of palm as the utmost potential crop for biodiesel production in Brazil [36]. The biodiesel production route via palm oil can be divided in agriculture and transportation stages and in the biodiesel production plant. The plant comprises an oil extraction and purification unit, a biodiesel production unit, a water treatment unit and a utilities plant (See Appendix A.2). Fig. 6 shows the representation of different stages through which the fresh fruit bunches (FFB) passes in the biodiesel production route, used to calculate the accumulated unit exergy and CO_2 emission costs of the biodiesel and its by-products (glycerol). The different fresh fruit bunches (FFB) streams are labeled by using a letter based on the previous stage, i.e., FFB followed by “A” stands for the stream leaving the agriculture process, whereas a letter “T” represents a stream leaving transportation stage.

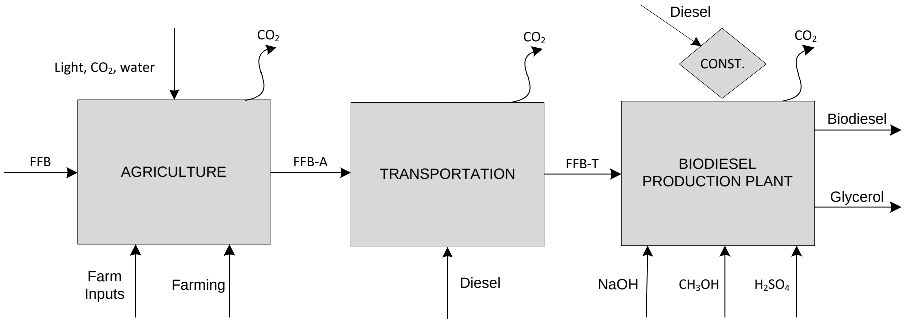

Fig. 6. Biodiesel production route (CONST, construction stage).

Natural resource inputs in the agriculture stage such as solar energy, water and CO_2 absorbed by the plant are considered to be equal to the mass, energy and exergy embodied in the biomass of the FFB. Thus, the only irreversibilities emerged from agriculture activities are considered as those related to the use of non-renewable energy sources such as fertilizers, pesticides and diesel oil in agriculture activities [37]. By considering that FFB are composed of oil (26%), water (49%), and fiber (25%), the chemical composition of the FFB is used to calculate the chemical exergy (16268kJ/kg_{FFB}) and φ value (1.0736) thereof. The approximate chemical composition of biodiesel derived from palm oil ($C_{18}H_{35}O_2$) allows determining the chemical exergy (39128 kJ/kg) and the φ value (1.0484) of this fuel [38,39]. For the Brazilian case, herbicides and irrigation systems make only a small contribution to the energy consumption, as adult palms are not irrigated and herbicides are used only sporadically in isolated crop areas a few times per year [40]. Then, the major fossil exergy consumption (2.85 MJ/$kg_{biodiesel}$) comes from other inputs such as natural gas for fertilizers production (29.3%), diesel oil for farming (64.2%), and transportation of raw material (4.4%). Table 3 presents the unit exergy and CO_2 emission costs of the different streams along the biodiesel production route. These values are used as input data in exergoeconomy analysis for the biodiesel plant stage. On the other hand, by considering a biodiesel production plant with a lifetime of 20 years, the energy required to build the plant and equipment is reported as 0.732MJ/$kg_{biodiesel}$ [41], which represents less than 5% of the energy consumption in the lifetime of the plant. Assuming that this energy is provided by diesel oil and taking into account that φ_{diesel}=1.0662, the exergy consumption is calculated as r = 0.0115kJ/kJ_{FBB}, whereas related direct CO_2 emissions results m_{CO2} = 0.0008 gCO_2/kJ_{CFF}.

Table 3. Unit exergy costs and CO_2 emission cost of the different FFB streams along the biodiesel production route.

Stream	**c_T (kJ/kJ_{FFB})**	**c_R (kJ/kJ_{FFB})**	**c_{NR} (kJ/kJ_{FFB})**	**c_{CO2} (gCO_2/kJ_{FFB})**
FFB	1.0000	1.0000	0.0000	0.0000
FFB-A	1.0362	1.0000	0.0362	0.0024
FFB-T	1.0384	1.0001	0.0383	0.0026

After FFB arrive at the biodiesel production plant, a sterilization process by using saturated steam at 3bar during 60 minutes is performed. Sterilization of FFB is necessary for deactivating enzymes responsible for oil splitting in free fatty acids (FFA), facilitating the digestion by weakening the pulp structure of the fruits and helping in the threshing process [42]. Thereafter, the fruits (mesocarp, fiber and nut) are conveyed to a digester where they are softened and converted into a homogenous mash, while the empty fruit bunches (stems) are returned to the plantation or used as boiler fuel. The mash is transferred to a twin screw press where oil is extracted, and the press cake and liquor (composed of oil, water and impurities) are separated. Electricity consumption in extraction process is the largest in the biodiesel production plant and reaches 9kWh/t_{FFB} [38]. The oil present in the liquor is clarified by removing the sludge in sedimentation tanks. The clarified phase is sent to centrifugal clarification and then goes through a vacuum dryer to reduce the moisture content in order to slow down hydrolysis and oxidation. On the other hand, the nuts and fibers are recovered, dried and subsequently separated from each other by using a cyclone system. By cracking the nuts, the shells and kernels are separated. Fiber and shells can be used as fuel in utilities plant, whereas the kernel is used for palm kernel oil extraction [38]. Total steam consumption in FFB pre-treatment, oil extraction and separation unit is 446 kg/t_{FBB}, whereas work consumption is 90,000 kJ/t_{FBB} (25kWh/t_{FBB}). Biodiesel is produced by transesterification of the vegetable oil, where triglycerides (TG) of cleaned oils are mixed with methanol (CH_3OH) and a catalyst (usually sodium hydroxide, NaOH), causing the oil molecules to break apart and reform into methyl esters (ME) and glycerol (G), according to (R.1). Transesterification reactor requires continuous stirring at 60ºC for 1 hour, using heat provided by saturated steam at 3bar [38]. Conversion efficiency of transesterification process reaches 95-99% depending on the quantity of FFA present in the oil [42]. Glycerol is then separated and the obtained methyl esters compose the biodiesel produced [1]:

$$TG + 3CH_3OH \overset{NaOH}{\longleftrightarrow} 3ME + G \qquad (R.1)$$

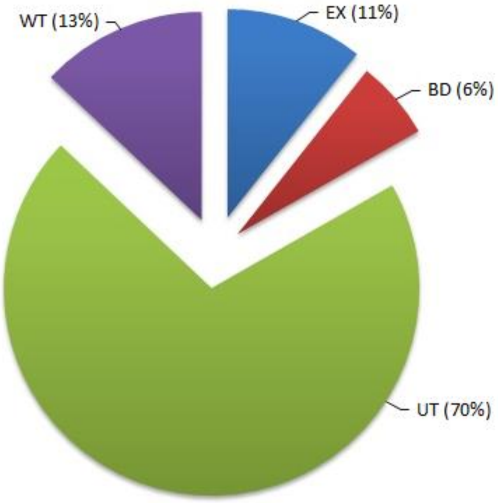

Fig.7. Percentage distribution of destroyed exergy at different units in the biodiesel production plant. EX, oil extraction and pretreatment unit; BD, biodiesel production unit; WT, water treatment unit; UT, utilities plant.

According to Fig. 7, the utilities plant is responsible for 70% of destroyed exergy, mainly due to highly irreversible process such as chemical reactions in biomass-fired boilers and heat exchange with finite temperature differences in the cogeneration plant. Water treatment unit is the second largest contributor to exergy destruction, since that unit consumes a large quantity of exergy with the only useful effect of removing water pollutants, without an appreciable modification of the exergy of the substances. Oil extraction and biodiesel production unit present a lower quantity of destroyed exergy because of the high efficiency of oil extraction and transesterification processes [38,39]. As a conclusion, the renewable and non-renewable unit exergy costs of biodiesel production are $1.0996 kJ/kJ_{biodiesel}$ and $0.4084 kJ/kJ_{biodiesel}$, respectively, whereas CO_2 emission cost is calculated as $0.0249 gCO_2/kJ_{biodiesel}$ (or $866 kgCO_2/m^3_{biodiesel}$). This result is close to that reported for biodiesel production as $864 kgCO_2/m^3_{biodiesel}$ [40-43]. Thus, the ratio between the renewable and non-renewable unit exergy cost for biodiesel production from palm oil is $c_R/c_{NR}=2.69$.

5. Ethanol production route

Ethanol production in Brazil relies entirely on sugar cane (14.5% sucrose, 13.5% fiber or bagasse, 2% soluble solids and 70% water), whereas cane bagasse represents 83% of the total biomass-based electricity generation capacity [44]. More than 70% sugar cane mills operate using an annexed plant scheme with simultaneous production of sugar and ethanol [45]. The most common configuration of utilities plants are based on cogeneration Rankine cycles using bagasse-fired boilers (22bar/300°C), able to entirely supply the energy demand of the mill, and still produce a surplus of bagasse (5-10% of biomass) and electricity to the grid (0-10 kWh/tc) [4,45]. A back-pressure steam turbine of two stages produces the electricity consumed in the whole plant and the surplus electricity, whereas another turbine produces solely the mechanical power used in the milling process [46]. Cogeneration power plant efficiency achieves 15-17% [47]. Figure 8 shows the different stages used to calculate the accumulated unit exergy and CO_2 emission costs of the ethanol and other products of the sugar cane mill. The cane streams are labeled by using a letter based on the previous stage, i.e., the letter “A” means the stream is leaving the agriculture process, whereas “T” indicates the stream is leaving the transportation stage. The processing units of the mill are classified as cane washing and milling (juice extraction), juice clarification and concentration, syrup crystallization and sugar refinement, must fermentation, wine distillation, collection and cooling of condensates, and the utilities plant, where the steam, electricity and mechanical power used in the units of the mill are produced (See Appendix A.3).

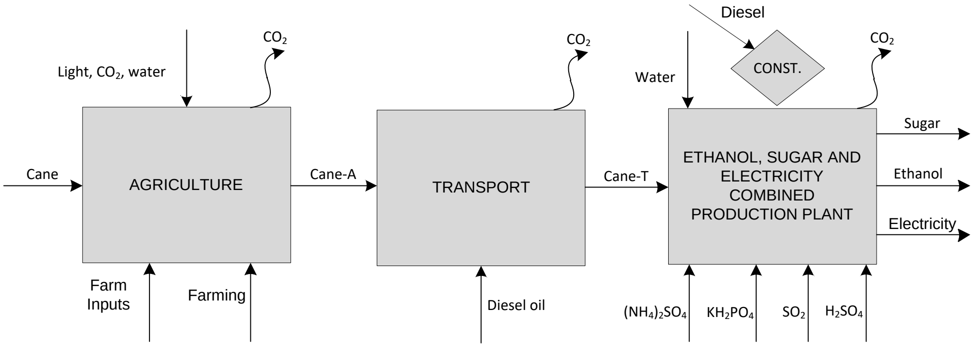

Fig.8. Combined production route of ethanol, sugar and electricity (CONST, construction stage).

The non-renewable energy consumption for the ethanol production is reported as 147kJ/MJ$_{\text{ethanol}}$, distributed between the consumption of natural gas to produce fertilizers (27%) and diesel consumption in sugar cane transportation and farming (73%) [45]. The yield of anhydrous ethanol, reported as 68.3 kg per ton of cane (tc) (or 86.3 L/tc) [4], together with the lower heating value (LHV) and φ for natural gas (1.0325), diesel oil (1.0662), sugar cane (1.1880) and ethanol (1.0319) are used to trace back the total and non-renewable exergy costs as well as the CO_2 emission cost of the sugar cane, along the agriculture and transportation stages. This data is summarized in Table 4. These values are used as input data in exergoeconomy analysis for sugar cane mill stage.

Table 4. Unit exergy costs and CO_2 emission cost of substances along the upstream processes of ethanol production route from sugar cane.

Stream	**LHV (kJ/kg)**	**c_T (kJ/kJ$_{cane}$)**	**c_R (kJ/kJ$_{cane}$)**	**c_{NR} (kJ/kJ$_{cane}$)**	**c_{CO2} (gCO$_2$/kJ$_{cane}$)**
Cane	4438	1.0000	1.0000	0.0000	0.0000
Cana-A	4438	1.0514	1.0000	0.0514	0.0034
Cana-T	4438	1.0590	1.0000	0.0590	0.0039
Natural gas	47330	1.0550	0.0000	1.0550	0.0023
Diesel oil	42350	1.0382	0.0008	1.0374	0.0033
Water	-	1.0000	1.0000	0.0000	0.0000

After the cane reaches the mill, it is conveyed and washed, in order to remove rocks, stalks and impurities that it may contain. Then, the cane is prepared using rotary blades in order to enhance the juice extraction, for which imbibition water is also added. In the extraction process unit, fiber and juice (sucrose, water and dissolved solids) are separated by using four tandem mills composed of three milling rolls powered by mechanical driving (16 kWh/tc) supplied by utilities plant [38, 46]. After extraction, bagasse (48-52% humidity) can be used as fuel at the cogeneration plant. Thereafter, in the juice clarification processes, lime is added to the juice in order to flocculate solid impurities, remove dissolved gases, reduce viscosity and perform the juice sterilization. The decanted residue of clarification (mud) is taken to a rotary vacuum filter (0.24-0.78 bar) where it is mixed with fine bagasse (bagacillo) and imbibition water to recover the sucrose, so conforming the filter cake which can be used as a crop fertilizer. Next, clarified juice is sent to concentration process unit, which consists of a vacuum evaporation system composed of five sequential Robert type evaporators. Steam produced in the first evaporator is used to heat the juice in the next one, reducing the steam consumption in the plant. The juice preheater and the first heat exchanger are fed with saturated steam (2.5bar) supplied by cogeneration plant. The steam produced in the first heat exchanger, or vegetable steam (1.7bar), is used in the second one as well as in other processes (clarification, crystallization and sugar refinement). Finally, concentrated juice or syrup (65 ºBrix[4]) is sent to crystallization units, where batch vacuum evaporators are used to obtain the massecuite (saturated sugar solution and sugar crystals), and then it is conduced to centrifugal separation process, where sucrose crystals are separated from saturated solution (molasses). This solution is evaporated and centrifuged until molasses exhaustion is achieved (95 ºBrix, 23 purity), when it can be used for ethanol production by mixing it with clarified juice and syrup. Meanwhile, raw sugar is dissolved again until 65ºBrix, decanted, vacuum evaporated, and centrifuged. Then, refined sugar is dried, packed and stored. Some chemicals, such as ammonium sulfate $(NH_4)_2SO_4$, mono potassium phosphate KH_2PO_4, as well as a blend of yeast milk and sulfuric acid are added to molasses, syrup and clarified juice mixture, in order to obtain the must that will be sent to fermentation vats. By keeping the temperature at 33ºC and anaerobic conditions in a Melle-Boinot batch, yeast (*Saccharomyces Cerevisiae*) converts reduced sugars into ethanol and CO_2, according to (R.2) [47]:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 + 7kcal \rightarrow 4C_2H_5OH + 4CO_2 + 54kcal \qquad (R.2)$$

Fermentation process efficiency achieves 91%, although other chemical compounds such as aldehydes, heavy oils and fusel oil can also be formed. After the fermentation, the mixture is centrifuged, separating the yeast, while the wine is sent to the distillation process unit. Distilled and rectified hydrated ethanol is produced in separate distillation columns. If necessary, anhydrous ethanol is obtained in a third column used to split the azeotrope and obtain a 99.9%v/v alcohol. The energy consumption for the mill and machinery construction is reported as 43MJ/tc [5]. Considering diesel oil (φ=1.0662) as the exergy consumption source used for the construction stage and the exergy embodied in machinery, along with the chemical exergy of cane (5273kJ/kg), then the exergy consumption and direct CO_2 emissions are calculated as r=0.0082kJ/kJ$_{cane}$ and m_{CO2}=0.0006 gCO_2/kJ$_{cane}$. According to Fig. 9, utilities plant account for 62% of the exergy destruction, mainly due to biomass burning as fuel and the low energy conversion efficiencies in the low pressure Rankine cycles. Fermentation reaction of ethanol and CO_2 production also contribute with about 21.2% of destroyed exergy, so better control of fermentation vat temperatures can enhance the performance of this process [46]. Exergy destruction in washing and milling process unit is related to sucrose loss in the bagasse, as well as to high power consumption of low efficiency equipment, such as direct driving turbines, commonly employed in Brazilian sugar cane mills.

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[4] 1 degree Brix corresponds to 1 g of sucrose per 100 g of juice.

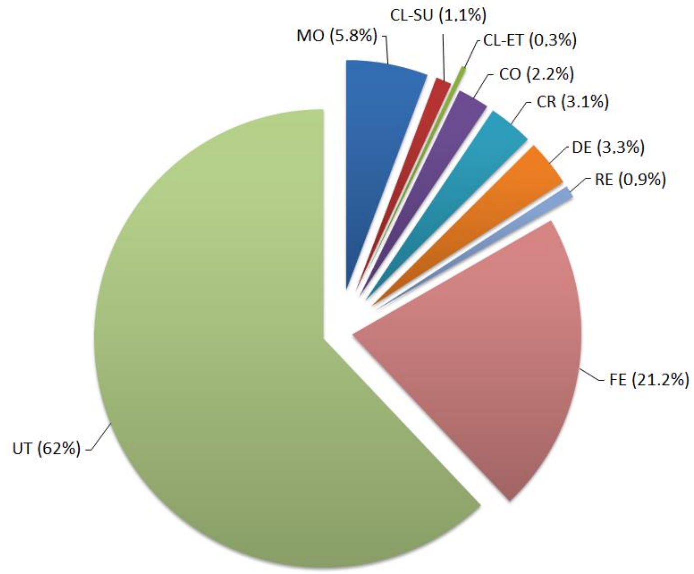

Fig.9. Percentage distribution of destroyed exergy at different units of sugar cane mill. CL, clarification unit for sugar (SU) or ethanol (ET) production; CO, concentration unit; CR; crystallization and sugar refinement; DE, distillation unit; FE, fermentation unit; MO, washing and milling unit; RE, condensates cooling unit; UT, utilities plant.

Renewable and non-renewable unit exergy costs of the different products of sugar cane mill are shown in Table 5, which closely agree with those reported in [47]. The high cost of electricity is a consequence of the low energy conversion efficiency and large exergy destruction of the cogeneration plant.

Table 5. Renewable and non-renewable unit exergy cost of the different products of sugar cane mill.

Product	c_T **(kJ/kJ)**	c_{NR} **(kJ/kJ)**	c_{CO2} **(gCO_2/kJ)**	c_R/c_{NR}
Refined sugar	1.9550	0.1129	0.0083	16.32
Ethanol	3.0560	0.1802	0.0127	15.96
Surplus Electricity (9.2kWh/tc)	6.6230	0.3658	0.0246	17.10

Obtained CO_2 emission cost of ethanol production is $0.0127 gCO_2/kJ_{ethanol}$ (or $300.12 kgCO_2/m^3_{ethanol}$), ranging between $269\text{-}345 kgCO_2/m^3_{álcool}$ reported by [4,45]. It is worth to notice that, since the CO_2 emitted in fermentation process (30.96 $kgCO_2$/tc or $754 kgCO_2/m^3_{etanol}$) is derived from sugar cane biomass and recycled in sugar cane growing, it is not considered as atmospheric net CO_2 emissions. Finally, by considering all the sugar cane mill products, mean c_R/c_{NR} ratio is calculated as 16.

6. Electricity Generation in Brazilian Electricity Mix

In Brazil, the total electricity demand in 2011 was approximately 567 TWh including the net imports (about 35.9 TWh), accounting for 18.1% of total energy consumption and approximately 8.0% of national CO_2 emissions. The integrated Brazilian electricity mix is dominated by hydroelectricity (81.9%) and biomass cogeneration plants (6.6%), followed by natural gas (4.4%), nuclear (2.7%) and oil products (2.5%), with coal products playing a much smaller role (1.4%). Wind power undergoing recent developments still represents only 0.5% of electricity mix [6]. The renewable ($1.4627 kJ/kJ_e$) and non-renewable ($0.3328 kJ/kJ_e$) unit exergy costs and CO_2 emission cost (62.63 gCO_2/kWh) of the electricity generation in Brazil, as reported by [23], were calculated by using a weighted average of the renewable and non-renewable unit exergy costs and CO_2

emission cost of the electricity generated in each route, according to the national electricity mix profile [6]. Those values are useful to compare the utilization of electricity and other energy sources at the end use stages, such as transportation, residential and industrial sectors.

7. Discussion

In Fig. 10, a comparison between the renewable and non-renewable unit exergy costs and CO_2 emission cost in the production of the fuels used in transportation sector is shown.

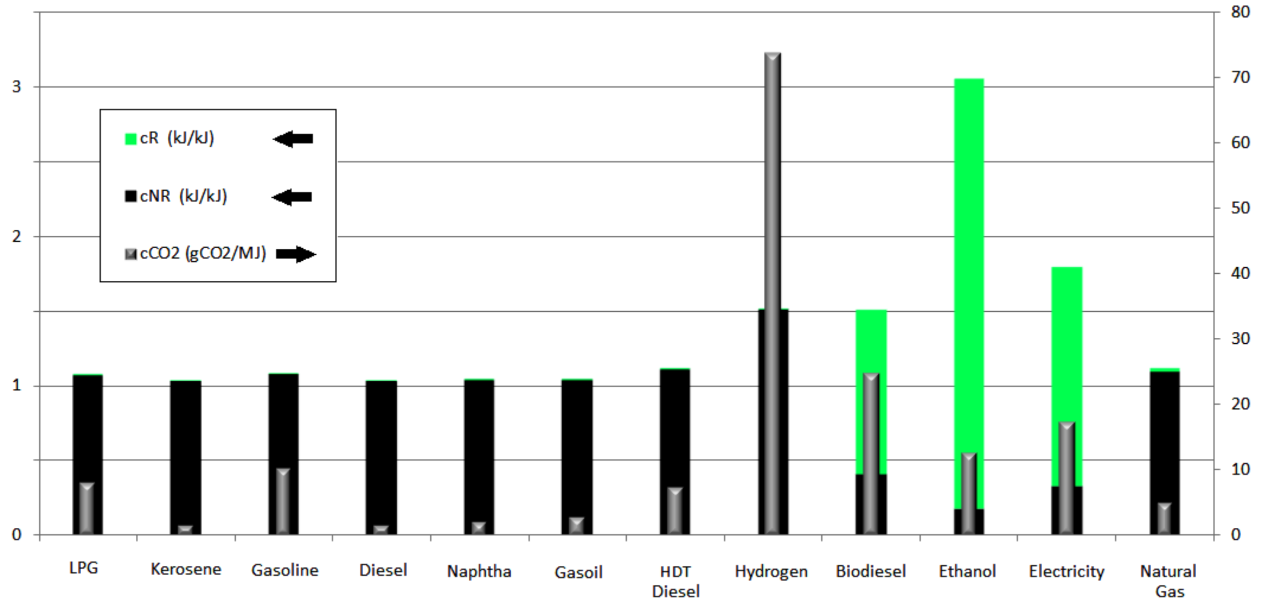

Fig. 10. Comparison between the renewable and non-renewable unit exergy costs and CO_2 emission cost of the different fuels used in transportation sector.

As it can be seen in Fig. 10, even though petroleum-derived fuels and natural gas show the lowest total unit exergy cost, most of such cost is non-renewable, c_R/c_{NR}~0. Among the petroleum derivatives, gasoline, LPG and hydrotreated diesel present the largest CO_2 emissions, because of the further processing, if compared with the products of combined distillation unit. Meanwhile, hydrogen unit exergy cost is approximately 25% greater than that of natural gas and other petroleum-derived fuels, besides showing the largest CO_2 emission cost. Indeed, as hydrogen is produced from non-renewable sources, such as energy intensive SMR process, the benefits of its use over natural gas (and gas-to-liquid derivatives) in transportation sector, in terms of logistic, distribution, technological limitations and safety is still questioned [48,49]. On the other hand, despite that the largest unit exergy costs correspond to biofuels and electricity, the largest proportion of these costs is renewable. For instance, a high share of hydropower and biomass electricity generation makes a large proportion of the unit exergy cost of the Brazilian electricity to be renewable (c_R/c_{NR}=4.39). Furthermore, the ratio between renewable to non-renewable unit exergy cost for sugar cane ethanol is calculated as c_R/c_{NR}=15.96, whereas for biodiesel, that figure is 2.69. However, as far as traditional cogeneration plants still persist in Brazil, it is possible to increase the conversion efficiency of utilities plant by using advanced technologies such as bagasse integrated gasification combined cycles (BIGCC) or supercritical cycles [47], reducing the costs of the different products of the mill. It is also worth to notice that, among the biofuels, ethanol presents the lowest non-renewable unit exergy costs, partly because of the distribution of unit exergy costs and CO_2 emission cost of ethanol production between the sugar and electricity generated. Thus, in autonomous distilleries, CO_2 emissions related to ethanol production could be higher depending on the amount of ethanol produced. Regarding palm oil biodiesel, CO_2 emission costs are appreciably increased because of the use of energy-intensive fossil inputs, such as methanol and sodium hydroxide. Since methanol is still produced from natural gas, methanol-based transesterification process produces more CO_2 emissions than if it was yielded using bioethanol [26, 38-42]. It is very important to point out that, at this extent, the CO_2 emissions shown in Fig. 10 do not take into account the analysis of fuel distribution and the end-use applications in transportation sector (i.e. direct burning of liquid or gaseous fuels in internal combustion engines, electricity utilization in battery-powered vehicles or hydrogen consumption in fuel cells). If direct CO_2 emissions for those activities were accounted for, the CO_2 emission cost for the fossil fuels would increase further, probably surpassing the emissions related to biofuel and electricity production. Besides, it is reasonable to expect that other technological, economic, social and political issues can influence the choice of fuels production, but those issues are out of the scope of this work. Finally, it is emphasized that whatever the primary energy source, either renewable or fossil, all of them are kinds of solar energy storage. The only difference is the time scale on which they are produced. While biofuels capture solar energy in a relatively small time scale, petroleum reservoirs represent a process that occurs in a geological time scale. This difference in the dynamic of the solar energy storage is the key of our definition of renewable and non-renewable energy [26]. According to this, considering an scenario for which the exploitation rate of the primary energy sources could not be continued indefinitely at the current energy consumption rate or, as well, by using low efficiency technologies, then the sustainability could not be guaranteed even for “renewable” energy sources or any of those studied in this work.

8. Conclusion

In this work, an exergy and environmental comparison between the fuel production routes for transportation sector in Brazil, including fossil fuels, biofuels and electricity generation is presented. Renewable and non-renewable unit exergy and CO_2 emission costs are calculated and the R/NR invested exergy ratios (c_R/c_{NR}) for biodiesel (2.69), electricity (4.39), and ethanol (15.96) are calculated. As a result, it was found that fossil fuels require the lowest exergy investment for the entire production chain, including oil and natural gas extraction, transportation, oil refining and natural gas treatment. In spite of this, the renewable fraction of the invested exergy is almost negligible, whereas the CO_2 emission cost will depend on the level of processing of the fuel. On the other hand, besides the subsidies and governmental policies required to renewable fuels scale up, other improvements on biofuels production routes, such as a higher efficiency of cogeneration power plants and the defossilization of the exergy consumption at the upstream agriculture and transportation stages, are required. In this way, lower unit exergy costs of ethanol and electricity could be achieved by (i) using biomass derivatives such as biofuels to carry out the farming activities, (ii) promoting the organic fertilization, using the residual biomass of the different cultures, and (iii) replacing the traditional cogeneration technologies at the Brazilian sugar cane mills (introducing BIGCC or supercritical cycles). Regarding hydrogen used as a transportation fuel, as far as it depends on fossil fuels for its production, the cost-benefit, security, energy density and environmental impacts suggest that other fossil sources such as natural gas or petroleum derivatives may accomplish a better performance.

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Nomenclature

c unit exergy cost (kJ/kJ)
B exergy rate or flow rate (kW)

b specific exergy (kJ/kg)
CNG compressed natural gas
E energy (kJ)
EEA extended exergy accounting
ELCA extended life cycle analysis
EV electric vehicles
E/W electricity (kWh) or mechanical power (kW)
GHG greenhouse gases
I fuel carbon content (% weight)
I/O input to output energy ratio
LCA life cycle analysis
LHV lower heating value
LCI life cycle inventory
m specific direct CO_2 emissions (gCO_2/kJ)
M direct CO_2 emissions (gCO_2/s)
PHEV plug-in hybrid electric vehicle
r exergy consumption (kJ/kJ)
R_m molecular mass ratio between carbon dioxide and elemental carbon (kg/kg)
T temperature, °C, K
tc ton of cane
v/v volume fraction

Greek symbols

η efficiency
φ ratio between the chemical exergy (b^{CH}) and lower heating value (LHV)

Subscripts and superscripts

C Fuel Consumption
CH chemical exergy
CO_2 carbon dioxide
en energy
ex exergy
F Processed fuel
i i-th supply stage consumption
j j-th transformation stage consumption
k k-th supply stage input
k+1 k-th supply stage output
l k-th transformation stage input
n end use stage
NR non-renewable
0 initial step
P Produced fuel
PH physical exergy
r r-th transformation stage product
R renewable
reac non combustion-derived CO_2 emissions
s supply stage
T total
t transformation stage

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Appendix A

In this section, the schemes of the fuel production plants as well as the properties and unit exergy costs of the streams produced in each unit are depicted.

A.1. Petroleum refinery

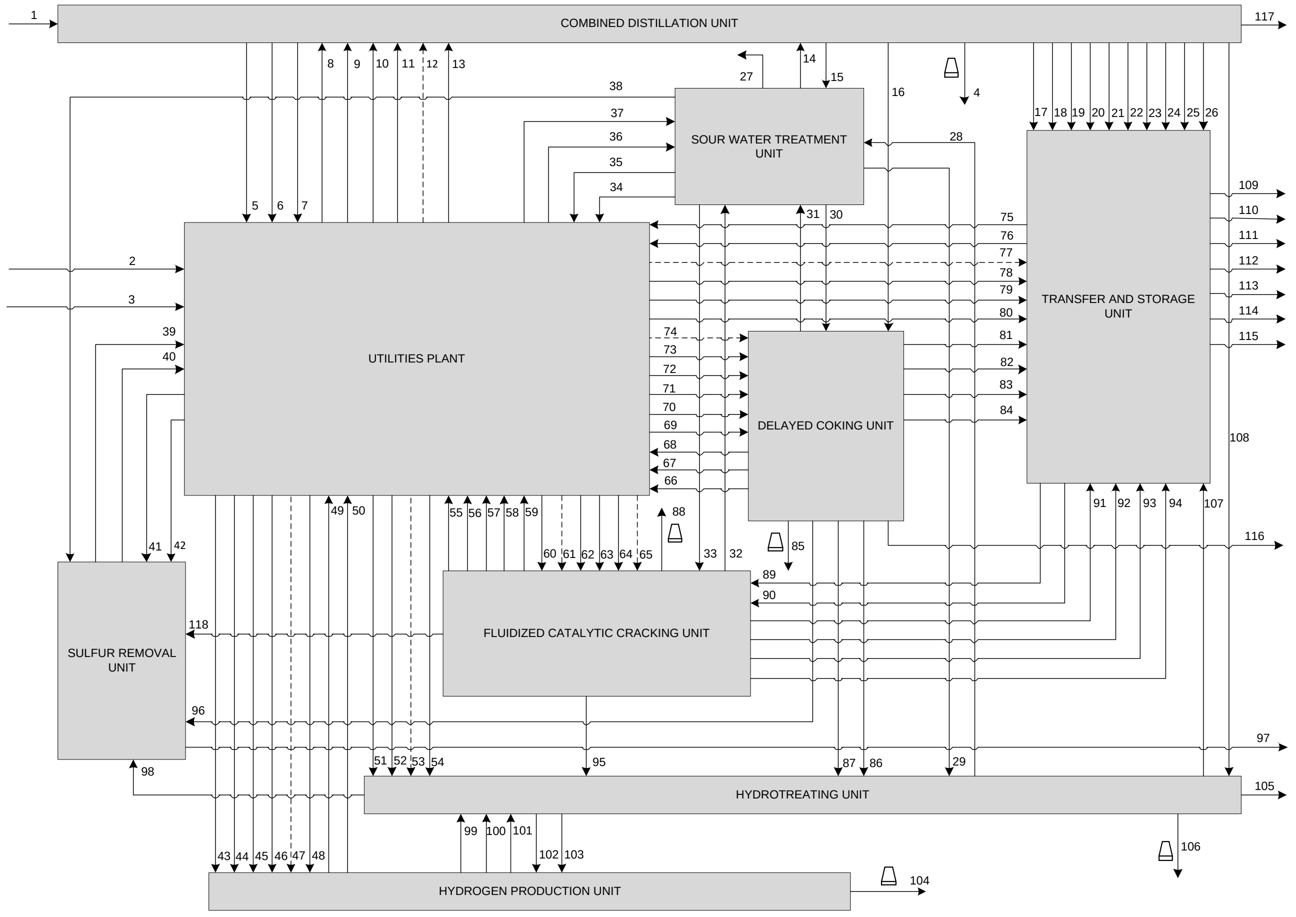

Fig A.1. Scheme of the petroleum refinery. Adapted from [32].

Table A.1. Thermal properties, unit exergy costs and CO_2 emission costs of the different streams in petroleum refinery units.

N°	**Name**	**T (°C)**	**P (bar)**	**m (kg/s)**	**B_T (kW)**	**b^{CH} (kJ/kg)**	**b^{PH} (kJ/kg)**	**c_T (kJ/kJ)**	**c_{NR} (kJ/kJ)**	**c_{CO2} (gCO_2/kJ)**
1	Crude Oil-TT	30	6.0	315.28	14121120	44789	0.55	1.0082	1.0075	0.0007
2	Natural Gas-TT	25	1.0	2.60	127062	48870	0.00	1.0550	1.0550	0.0023
3	Water	25	1.0	195.92	9796.13	50.00	0.00	1.0000	0.0000	0.0000
4	Heat	--	--	--	3593.94	--	--	--	--	--
5	Fuel Gas	36	5.0	1.68	82617.55	49143	42.82	1.0308	1.0298	0.0016
6	Condensate	25	1.0	0.00	0.00	50.00	0.00	2.1089	2.1069	0.0921
7	Low Pressure Steam	164	4.0	2.47	1855.37	50.00	701.16	1.0308	1.0298	0.0016
8	Compressed Air	--	--	0.3	56.63	--	--	5.0454	5.0424	0.2544
9	Fuel Gas	36	5.0	3.26	161045	49143	42.82	1.0737	1.0724	0.0082
10	Low Pressure Steam	165	4.0	7.56	5678.77	50.00	701.16	1.9491	1.9474	0.0804
11	Medium Pressure Steam	292	14	10.42	10612.25	50.00	968.45	2.1944	2.1922	0.0984
12	Electricity	--	--	--	6690.00	--	--	3.1818	3.1801	0.1626
13	Industrial Water	25	1.0	0.00	0.00	50.00	0.00	1.8810	1.8805	0.0453
14	Rectified Water	25	1.0	28.99	1449.63	50.00	0.00	1.0727	1.0716	0.0066
15	Sour Water	25	1.0	15.51	775.50	50.00	0.00	2.1089	2.1069	0.0921
16	Vacuum Residue	170	5.0	71.75	3103806	43261	56.46	1.0308	1.0298	0.0016
17	Heavy Gasoil	108	5.0	44.59	1971732	44215	19.82	1.0308	1.0298	0.0016
18	Light Gasoil	125	5.0	3.28	146059	44481	28.70	1.0308	1.0298	0.0016
19	Heavy Naphtha	25	1.0	12.43	582209	46854	0.00	1.0308	1.0298	0.0016
20	Liquefied Gas	39	5.0	1.21	60013	49562	72.64	1.0308	1.0298	0.0016
21	Kerosene	25	1.0	22.44	1037912	46253	0.00	1.0308	1.0298	0.0016
22	Heavy Diesel	163	5.0	12.82	574353	44789	36.33	1.0308	1.0298	0.0016
23	Light Diesel	125	5.0	66.18	3012217	45514	30.41	1.0308	1.0298	0.0016
24	Light Naphtha	25	1.0	20.82	988093	47465	0.00	1.0308	1.0298	0.0016
25	Vacuum Residue	172	5.0	25.62	1108275	43260	57.99	1.0308	1.0298	0.0016
26	Top Residual Gasoil	25	1.0	8.43	377141	44720	0.00	1.0308	1.0298	0.0016
27	Residual water	25	1.0	11.85	592.39	50.00	0.00	1.0727	1.0716	0.0066
28	Sour Water	25	1.0	10.70	535.00	50.00	0.00	3.8990	3.8974	0.1841
29	Rectified Water	25	1.0	7.56	378.23	50.00	0.00	1.0727	1.0716	0.0066
30	Rectified Water	25	1.0	7.15	357.25	50.00	0.00	1.0727	1.0716	0.0066
31	Sour Water	25	1.0	9.84	491.85	50.00	0.00	2.1014	2.0993	0.0913
32	Sour Water	25	1.0	26.67	1333.50	50.00	0.00	2.1766	2.1753	0.0731
33	Rectified Water	25	1.0	6.60	329.80	50.00	0.00	1.0727	1.0716	0.0066
34	Low Pressure Steam	165	4.0	0.21	160.18	50.00	701.16	2.1944	2.1922	0.0984
35	Condensate	95	4.0	12.10	969.63	50.00	30.15	2.1940	2.1918	0.0984
36	Low Pressure Steam	165	4.0	0.03	18.84	50.00	701.15	1.9491	1.9475	0.0804
37	Medium Pressure Steam	292	14	12.29	12512.94	50.00	968.45	2.1944	2.1922	0.0984
38	Sour Gas	98	1.48	0.57	10374.35	18178	32.97	1.0727	1.0716	0.0066
39	Low Pressure Steam	165	4.0	1.84	1379.41	50.00	701.16	1.4139	1.4125	0.0095

N°	Name	T (°C)	P (bar)	m (kg/s)	B_T (kW)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
40	Medium Pressure Steam	292	14	2.03	2067.00	50.00	968.45	1.0327	1.0317	0.0073
41	Medium Pressure Water	143	29	3.87	508.27	50.00	81.48	2.5523	2.5503	0.1032
42	Fuel Gas	25	6.0	0.03	1699.97	47978	260.63	1.0737	1.0724	0.0082
43	Compressed Air	--	--	0.30	56.63	--	--	5.0454	5.0424	0.2544
44	Natural Gas	24	30	2.52	124352	48870	464	1.0550	1.0550	0.0023
45	Medium Pressure Water	143	28	3.87	508.83	50.00	81.48	2.5523	2.5503	0.1032
46	High Pressure Water	143	117	15.29	2143.05	50.00	90.16	2.6721	2.6701	0.1100
47	Electricity	--	--	--	730.00	--	--	3.1818	3.1801	0.1626
48	Fuel Gas	25	6.0	0.27	13342.32	47978	388.12	1.0737	1.0724	0.0082
49	Low Pressure Steam	165	4.0	8.03	6034.82	50.00	701.16	1.5139	1.5137	0.0739
50	Condensate	95	4.0	12.96	1038.76	50.00	30.15	2.9875	2.9856	0.1289
51	Medium Pressure Steam	292	14	4.97	5061.70	50.00	968.45	2.1944	2.1922	0.0984
52	Fuel Gas	25	6.0	0.49	24020.61	47978	510.53	1.0737	1.0724	0.0082
53	Electricity	--	--	--	4080.00	--	--	3.1818	3.1801	0.1626
54	Compressed Air	--	--	0.30	56.62	--	--	5.0454	5.0424	0.2544
55	Condensate	95	4.0	15.95	1278.03	50.00	30.15	2.1766	2.1753	0.0731
56	Low Pressure Steam	165	4.0	1.19	893.88	50.00	701.16	1.0810	1.0799	0.0103
57	Fuel Gas	25	6.0	5.33	267255	47978	11532	1.0810	1.0799	0.0103
58	CO Gas	728	2.6	58.01	67963.71	--	--	1.0810	1.0799	0.0103
59	Medium Pressure Steam	292	14	17.03	17344.20	50.00	968.45	1.0810	1.0799	0.0103
60	Compressed Air	--	--	0.30	56.63	--	--	5.0454	5.0424	0.2544
61	Electricity	--	--	--	1716.00	--	--	3.1818	3.1801	0.1626
62	Medium Pressure Water	143	28	18.22	2395.57	50.00	81.48	2.5523	2.5503	0.1032
63	Industrial Water	25	1.0	36.02	1812.17	50.00	0.00	1.8810	1.8805	0.0453
64	Natural Gas	13	4.0	0.17	8408.42	48870	100	1.0550	1.0550	0.0023
65	Mechanical Power	--	--	--	17350.00	--	--	4.3900	4.3855	0.2147
66	Low Pressure Steam	165	4.0	1.60	1201.86	50.00	701.16	1.0726	1.0715	0.0037
67	Fuel Gas	35	1.4	2.62	125787	47978	31.79	1.0726	1.0715	0.0037
68	Condensate	95	4.0	11.67	935.65	50.00	30.15	2.1014	2.0993	0.0913
69	Compressed Air	--	--	0.30	56.63	--	--	5.0454	5.0424	0.2544
70	High Pressure Water	143	117	0.09	12.05	50.00	90.16	2.6721	2.6701	0.1100
71	Fuel Gas	25	1.0	1.26	60452.28	47978	0.00	1.0737	1.0724	0.0082
72	Low Pressure Steam	165	4.0	5.47	4108.85	50.00	701.16	1.9491	1.9475	0.0804
73	Medium Pressure Steam	292	14	10.41	10602.06	50.00	968.45	2.1944	2.1922	0.0984
74	Electricity	--	--	--	6390.00	--	--	3.1818	3.1801	0.1626
75	Condensate	95	4.0	0.0001	0.00815	50.00	31.50	1.9491	1.9475	0.0804
76	Gasoil	25	1.0	1.50	67069.83	44713	0.00	1.0456	1.0445	0.0036
77	Electricity	--	--	--	5575.00	--	--	3.1818	3.1801	0.1626
78	Natural Gas	25	1.0	0.06	2932.38	48870	0.00	1.0550	1.0550	0.0023
79	Low Pressure Steam	165	4.0	0.0001	0.08	50.00	701.16	1.9491	1.9475	0.0804

N°	**Name**	**T (°C)**	**P (bar)**	**m (kg/s)**	**B_T (kW)**	**b^{CH} (kJ/kg)**	**b^{PH} (kJ/kg)**	**c_T (kJ/kJ)**	**c_{NR} (kJ/kJ)**	**c_{CO2} (gCO_2/kJ)**
80	Compressed Air	--	--	0.3	56.63	--	--	5.0454	5.0424	0.2544
81	Liquefied Gas	35	1.3	2.16	103413	47805	57.56	1.0726	1.0715	0.0037
82	Light Naphtha	25	1.0	6.67	309966	46502	0.00	1.0726	1.0715	0.0037
83	Heavy Naphtha	205	2.75	2.60	116980	45063	85.89	1.0726	1.0715	0.0037
84	Heavy Gasoil	34	18	11.94	516482	43268	2.28	1.0726	1.0715	0.0037
85	Heat	--	--	--	426.77	--	--	--	--	--
86	Light Gasoil	194	18	12.56	565382	45011	84.82	1.0726	1.0715	0.0037
87	Medium Gasoil	187	18	17.06	748699	43880	69.39	1.0726	1.0715	0.0037
88	Heat	--	--	--	3141.91	--	--	--	--	--
89	Naphtha	25	1.0	17.31	813084	47081	0.00	1.0456	1.0445	0.0036
90	Gasoil	25	1.0	58.08	2552814	44114	0.00	1.0456	1.0445	0.0036
91	Light Cycled Oil	25	1.0	0.00	0.00	43739	0.00	1.0810	1.0799	0.0102
92	Decanted Oil	25	1.0	7.76	329421	42467	0.00	1.0810	1.0799	0.0102
93	Liquefied Gas	25	1.0	7.76	380265	49024	0.00	1.0810	1.0799	0.0102
94	Gasoline	25	1.0	42.38	1992087	47004	0.00	1.0810	1.0799	0.0102
95	Light Cycled Oil	37	1.0	7.09	309993	43739	0.45	1.0810	1.0799	0.0102
96	Sour Gas	35	1.4	0.10	1595.08	15877	182.74	1.0726	1.0715	0.0037
97	Sulfur	25	1.0	1.30	24899.99	19154	0.00	1.0928	1.0917	0.0075
98	Sour Gas	98	1.4	0.90	16418.60	18178	32.97	1.1129	1.1119	0.0074
99	Low Pressure Steam	165	4.0	18.06	13567.28	50.00	701.16	1.5139	1.5137	0.0739
100	Hydrogen	35	20	0.66	79499.36	117116	3796.6	1.5139	1.5137	0.0739
101	Medium Pressure Steam	292	14	4.46	4546.14	50.00	968.45	1.5139	1.5137	0.0739
102	Medium Pressure Steam	292	14	0.11	111.01	50.00	968.45	1.1129	1.1119	0.0074
103	Sour Water	25	1.0	24.25	1212.56	50.00	0.00	3.8990	3.8974	0.1841
104	Heat	--	--	--	6.34	--	--	--	--	--
105	Hydrotreated Diesel	25	6.2	58.59	2649372	45222	--	1.1129	1.1119	0.0074
106	Heat	--	--	--	1050.01	--	--	--	--	--
107	Wild Naphtha	25	1.0	0.16	7141.10	44632	0.00	1.1129	1.1119	0.0074
108	Heavy Diesel	163	5.0	22.28	997760	44789	54.44	1.0308	1.0298	0.0016
109	Liquefied Gas	25	1.0	11.13	543691	47805	0.00	1.0738	1.0728	0.0081
110	Kerosene	25	1.0	22.44	1037912	46253	0.00	1.0308	1.0298	0.0016
111	Gasoline	25	1.0	42.38	1992087	47004	0.00	1.0810	1.0799	0.0103
112	Vacuum Residue	25	1.0	25.62	1108275	43260	0.00	1.0308	1.0298	0.0016
113	Diesel Oil	25	1.0	79.01	3586570	45394	0.00	1.0308	1.0298	0.0016
114	Naphtha	25	1.0	25.36	1191305	46976	0.00	1.0400	1.0389	0.0021
115	Gasoil	25	1.0	16.42	721963	43969	0.00	1.0422	1.0412	0.0028
116	Coke	25	1.0	16.04	606319	37800	0.00	1.0726	1.0715	0.0037
117	Brine	25	1.0	30.74	1449.63	50.00	0.00	1.0308	1.0298	0.0016
118	Sour Gas	25	1.0	0.39	6158.04	15710	0.00	1.0809	1.0789	0.0103

A.2. Biodiesel production plant

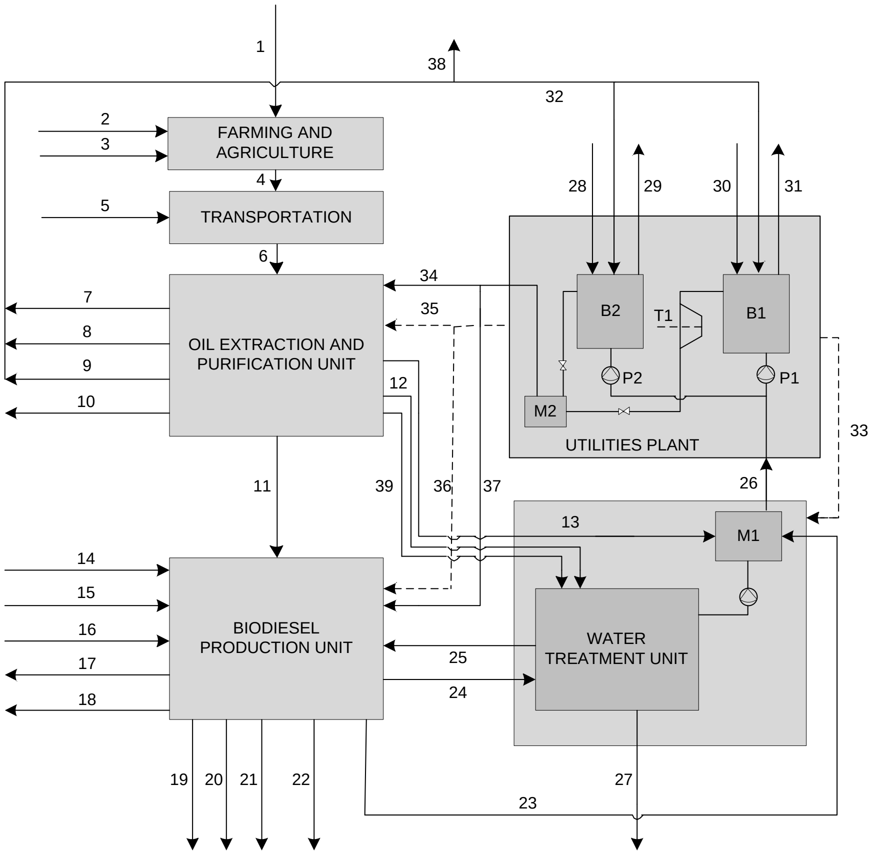

Fig A.2. Scheme of the biodiesel production plant.

Table A.2. Thermal properties, unit exergy costs and CO_2 emission costs of the different streams in biodiesel production plant.

N°	Name	T (°C)	P (bar)	m (kg)	B_T (kJ)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
1	FFB	25	1.0	1000	16268000	16268	0.00	1.0000	0.0000	0.0000
2	Natural Gas	25	1.0	--	--	48873	0.00	1.0550	1.0550	0.0023
3	Diesel Oil	25	1.0	--	--	45152	0.00	1.0382	1.0374	0.0033
4	FFB-A	25	1.0	1000	15839000	16268	0.00	1.0362	0.0362	0.0024
5	Diesel Oil	25	1.0	--	--	45152	0.00	1.0382	1.0374	0.0033
6	FFB-T	25	1.0	1000	15839000	16268	0.00	1.0384	0.0383	0.0026
7	Shells	25	1.0	68.00	1129000	16602.94	0.00	1.2480	0.0461	0.0031
8	Fibres	25	1.0	180.00	2260000	12555.56	0.00	1.2480	0.0461	0.0031
9	Stems	25	1.0	210.00	1536000	7314.29	0.00	1.2480	0.0461	0.0031
10	Kernels	25	1.0	52.00	2079000	39980.77	0.00	1.2480	0.0461	0.0031
11	Oil	25	1.0	210.00	8155560	38836	0.00	1.2480	0.0461	0.0031
12	Mixed Condensate	sat	3.0	220.43	25935.79	50.00	67.66	1.2480	0.0461	0.0031
13	Clean Condensate	sat,	3.0	195.59	23013.70	50.00	67.66	8.8340	0.3284	0.0220
14	H_2SO_4	25	1.0	2.96	4929	1666	0.00	1.8005	1.3504	0.0857
15	NaOH	25	1.0	2.42	4523.30	1873	0.00	18.1126	13.813	0.8619
16	CH_3OH	25	1.0	92.40	2070499	22408	0.00	1.7946	1.7946	0.1054

N°	**Name**	**T (°C)**	**P (bar)**	**m (kg)**	**B_T (kJ)**	**b^{CH} (kJ/kg)**	**b^{PH} (kJ/kg)**	**c_T (kJ/kJ)**	**c_{NR} (kJ/kJ)**	**c_{CO2} (gCO_2/kJ)**
17	CH_3OH	25	1.0	70.11	1571025	22408	0.00	1.5080	0.4084	0.0249
18	Na_2SO_4	25	1.0	5.37	700.30	130.31	0.00	0.00	0.0000	0.0000
19	Water loss	sat	1.0	8.40	4472.16	50.00	482.4	0.00	0.0000	0.0000
20	FFA	25	1.0	7.35	274831	37391.97	0.00	0.00	0.0000	0.0000
21	Glycerol	25	1.0	22.29	410208	18403.23	0.00	1.5080	0.4084	0.0249
22	Biodiesel	25	1.0	200.50	7845164	39128	0.00	1.5080	0.4084	0.0249
23	Clean Condensate	sat	3.0	167.49	19706.41	50.00	67.66	8.8340	0.3284	0.0220
24	Washing water	69,7	1.0	75.60	4745.41	50.00	12.77	1.5080	0.4084	0.0249
25	Washing water	25	1.0	84.00	4200	50.00	0.00	18.1200	0.7025	0.0469
26	Condensate	60	3.0	590.90	34431.15	50.00	8.27	18.1200	0.7025	0.0469
27	Residual Water	30	1.0	294.20	14710	50.00	0	18.1200	0.7025	0.0469
28	Air	25	1.0	506.60	0.00	0.00	0.00	0.0000	0.0000	0.0000
29	Flue Gas	--	1.0	612.40	118561	98.90	94.70	0.0000	0.0000	0.0000
30	Air	25	1.0	680.20	0.00	0.00	0.00	0.0000	0.0000	0.0000
31	Flue Gas	--	1.0	822.20	159178	98.90	94.70	0.0000	0.0000	0.0000
32	Biomass	25	1.0	258.20	3242476	12558	0.00	1.2480	0.0461	0.0031
33	Electricity	--	--	--	1048.38	--	--	8.8340	0.3284	0.0220
34	Steam	sat	3.0	446.00	309970	50.00	645	8.8340	0.3284	0.0220
35	Electricity	--	--	--	90000	--	--	8.8340	0.3284	0.0220
36	Electricity	--	--	--	11340	--	--	8.8340	0.3284	0.0220
37	Steam	sat	3.0	167.50	116413	50.00	645	8.8340	0.3284	0.0220
38	Residual Biomass	25	1.0	199.80	2509088	12558	0.00	1.2480	0.0461	0.0031
39	Sludge	25	1.0	310.00	433038	1396.90	0.00	1.2480	0.0461	0.0031

FFA: Free Fatty Acids

A.3. Ethanol production plant

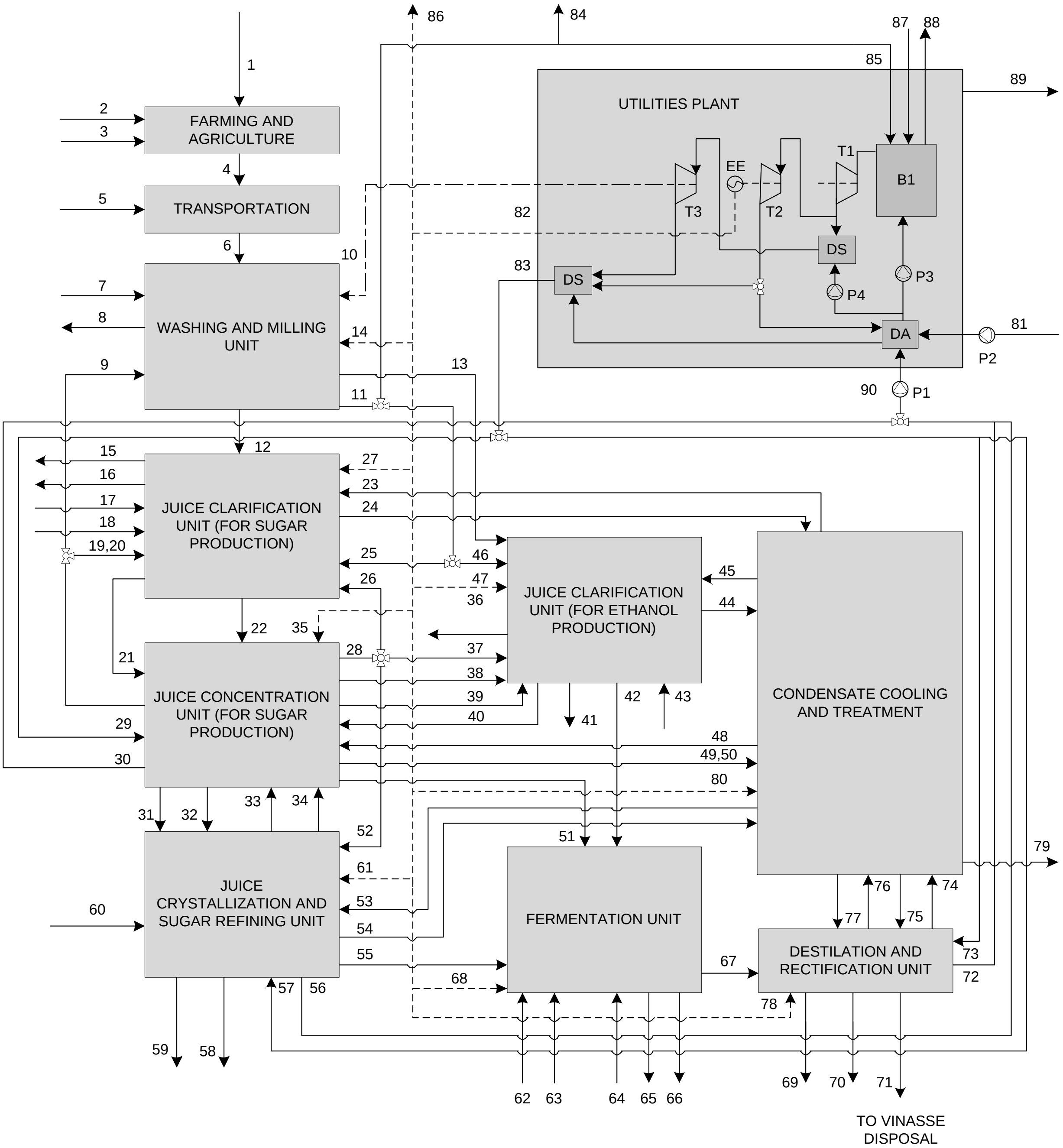

Fig A.3. Scheme of ethanol, sugar and electricity combined production mill. Adapted from [46].

Table A.3. Thermal properties, unit exergy costs and CO_2 emission costs of the different streams in sugar cane mill.

N°	Name	T (°C)	P (bar)	m (kg/s)	B_T (kW)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
1	Cane	25	1	138.90	732420	5273	0.00	1.0000	0.0000	0.0000
2	Natural Gas	25	1	--	--	48873	0.00	1.0550	1.0550	0.0023
3	Diesel	25	1	--	--	45152	0.00	1.0382	1.0374	0.0033
4	Cane-A	25	1	138.90	732420	5273	0.00	1.0514	0.0514	0.0034
5	Diesel	25	1	--	--	45152	0.00	1.0382	1.0374	0.0033
6	Cane-T	25	1	138.90	732420	5273	0.00	1.0590	0.0590	0.0040

N°	Name	T (°C)	P (bar)	m (kg/s)	B_T (kW)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
7	Washing water	25	1	37.00	1850	50.00	0.00	1.0000	0.0000	0.0000
8	Washing Water	25	1	37.00	1850	50.00	0.00	0.0000	0.0000	0.0000
9	Imbibition Water	50	6	41.70	2278.91	50.00	4.65	1.8240	0.1054	0.0077
10	Mech. Power	--	--	--	8000	--	--	6.6230	0.3685	0.0246
11	Bagasse	25	1	38.90	388416.5	9985	0.00	1.1610	0.0647	0.0043
12	Juice (Sugar)	35	6	98.80	272336.3	2755	1.44	1.1610	0.0647	0.0043
13	Juice (Ethanol)	35	6	42.90	118251.3	2755	1.44	1.1610	0.0647	0.0043
14	Electricity	--	--	--	1200	--	--	6.6230	0.3685	0.0246
15	Flash Steam	97	0.9	1.5	783	50.00	472	0.0000	0.0000	0.0000
16	Filter Cake	25	1	3.40	7350.8	2162	0.00	1.2160	0.0717	0.0055
17	SO_2	25	1	0.10	489.20	4892	0.00	2.0379	1.5542	0.4634
18	CaO	25	1	0.10	196.51	1965.05	0.00	2.6049	1.9866	0.2379
19	Water	107.4	6	2.20	200.20	50.00	41.00	1.8240	0.1054	0.0077
20	Water	107.4	6	6.80	618.80	50.00	41.00	1.8240	0.1054	0.0077
21	Condensate	sat	1.7	14.10	1381.80	50.00	48.00	1.8240	0.1054	0.0077
22	Clarified Juice	97	6	103.20	273996	2625	30.00	1.2160	0.0717	0.0055
23	Water Bar. Condenser	30	1	8.67	442.17	50.00	1.00	1.8240	0.1054	0.0077
24	Water Bar. Condenser	50	1	8.92	490.60	50.00	5.00	1.2160	0.0717	0.0055
25	Bagasse	25	1	0.50	4992.50	9985	0.00	1.1610	0.0647	0.0043
26	Vegetable Steam	sat	1.7	14.10	8637.66	50.00	562.60	1.8240	0.1054	0.0077
27	Electricity	--	--	--	627	--	--	6.6230	0.3685	0.0246
28	Vegetable Steam	sat	1.7	34.20	20950.92	50.00	562.60	1.8240	0.1054	0.0077
29	Steam	sat	2.5	47.70	31863.60	50.00	618.00	6.6230	0.3685	0.0246
30	Condensate	sat	2.5	47.70	5294.70	50.00	61.00	6.6230	0.3685	0.0246
31	Syrup	58.7	0.16	20.90	238740.7	11416.74	6.26	1.8240	0.1054	0.0077
32	Dilution Water	107.4	6	4.16	378.56	50.00	41.00	1.8240	0.1054	0.0077
33	Condensate	sat	1.7	11.80	1156.40	50.00	48.00	1.9550	0.1129	0.0083
34	Condensate	sat	1.7	2.20	215.60	50.00	48.00	1.9550	0.1129	0.0083
35	Electricity.	--	--	--	900	--	--	6.6230	0.3685	0.0246
36	Flash Steam	97	0.93	0.70	365.40	50.00	472.00	0.0000	0.0000	0.0000
37	Vegetable Steam	sat	1.7	6.10	3736.86	50.00	562.60	1.8240	0.1054	0.0077
38	Water	107.4	6	1.00	91.00	50.00	41.00	1.8240	0.1054	0.0077
39	Water	107.4	6	2.90	263.90	50.00	41.00	1.8240	0.1054	0.0077
40	Condensate	sat	1.7	6.10	597.80	50.00	48.00	1.8240	0.1054	0.0077
41	Filter Cake	25	1	1.50	3243	2162	0.00	1.2110	0.0705	0.0049
42	Clarified Juice	97	6	44.90	119209.5	2625	30.00	1.2110	0.0705	0.0049
43	CaO	25	1	0.10	196.51	1965.05	0.00	2.6049	1.9866	0.2379
44	Water Bar. Condenser	50	1	3.90	214.50	50.00	5.00	1.2110	0.0705	0.0049
45	Water Bar. Condenser	30	1	3.80	193.80	50.00	1.00	1.8240	0.1054	0.0077
46	Bagasse	25	1	0.20	1997	9985	0.00	1.1610	0.0647	0.0043
47	Electricity	--	--	--	273.00	--	--	6.6230	0.3685	0.0246
48	Water Bar.	30	1	360.30	18375.30	50.00	1.00	2.7640	0.1609	0.0116

N°	Name	T (°C)	P (bar)	m (kg/s)	B_T (kW)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
	Condenser									
49	Water Bar. Condenser	50	1	370.20	20361	50.00	5.00	1.8240	0.1054	0.0077
50	Condensate	50	1	10.60	583.00	50.00	5.00	1.8240	0.1054	0.0077
51	Syrup	58.7	0.16	2.60	29699.80	11416.74	6.26	1.8240	0.1054	0.0077
52	Vegetable Steam	sat	1.7	14.00	8576.40	50.00	562.60	1.8240	0.1054	0.0077
53	Water Bar. Condenser	30	1	337.60	17217.60	50.00	1.00	1.8240	0.1054	0.0077
54	Water Bar. Condenser	50	1	347.40	19107.00	50.00	5.00	1.9550	0.1129	0.0083
55	Molasses	25	1	5.90	75661.60	12824	0.00	1.9550	0.1129	0.0083
56	Condensate	sat	2.5	0.20	22.20	50.00	61.00	6.6230	0.3685	0.0246
57	Steam	sat	2.5	0.20	133.60	50.00	618.00	6.6230	0.3685	0.0246
58	Drying air	90	1	4.30	26.83	0.00	6.24	0.0000	0.0000	0.0000
59	Dry Sugar	25	1	9.00	157967	17551.86	0.00	1.9550	0.1129	0.0083
60	Drying Air	25	1	4.30	0.00	0.00	0.00	0.0000	0.0000	0.0000
61	Electricity	--	--	--	1950	--	--	6.6230	0.3685	0.0246
62	Dilution Water	25	6	17.00	867	50.00	1.00	1.0000	0.0000	0.0000
63	KH_2PO_4	25	1	0.05	57.48	1061	0.00	9.6486	7.3583	0.4591
63	H_2SO_4	25	1	0.02	39.34	1666	0.00	1.8005	1.3504	0.0856
63	$(NH_4)_2SO_4$	25	1	0.02	118.08	5000.76	0.00	2.0647	2.0647	0.1213
64	Cooling Water	25	1	7.9	395	50.00	0.00	0.0000	0.0000	0.0000
65	Cooling Water	25	1	7.9	395	50.00	0.00	1.0000	0.0000	0.0000
66	CO_2	25	1	4.30	1941.84	451.59	0.00	0.0000	0.0000	0.0000
67	Wine	25	1	66.30	137307	2071	0.00	2.5680	0.1531	0.0109
68	Electricity	--	--	--	600	--	--	6.6230	0.3685	0.0246
69	Hydrated Ethanol	25	1	4.50	124290	27620	0.00	3.0560	0.1802	0.0127
70	Secondary Ethanol	25	1	0.20	5376.40	26882	0.00	3.0560	0.1802	0.0127
71	Vinasse	25	1	61.50	3075	50.00	0.00	3.0560	0.1802	0.0127
72	Condensate	sat	2.5	16.30	1809.30	50.00	61.00	6.6230	0.3685	0.0246
73	Steam	sat	2.5	16.30	10888.40	50.00	618.00	6.6230	0.3685	0.0246
74	Cooling Water	50	1	113.60	6248	50.00	5.00	3.0560	0.1802	0.0127
75	Cooling Water	30	1	113.60	5793.60	50.00	1.00	1.8240	0.1054	0.0077
76	Cooling Water	30	1	7.00	357	50.00	1.00	1.8240	0.1054	0.0077
77	Cooling Water	50	1	7.00	385	50.00	5.00	3.0560	0.1802	0.0127
78	Electricity	--	--	--	300	--	--	6.6230	0.3685	0.0246
79	Residual Water	45	1	31.30	1648.88	50.00	2.68	1.8240	0.1054	0.0077
80	Electricity	--	--	--	150	--	--	6.6230	0.3685	0.0246
81	Make Up Water	25	1	8.2	410	50.00	0.00	1.0000	0.0000	0.0000
82	Electricity	--	--	--	10225	--	--	6.6230	0.3685	0.0246
83	Steam	sat	2.5	63.7	42552	50.00	618.00	6.6230	0.3685	0.0246
84	Residual Bagasse	25	1	7.4	73889	9985	0.00	1.1610	0.0647	0.0043
85	Used Bagasse	25	1	30.8	307538	9985	0.00	1.1610	0.0647	0.0043
86	Surplus Electricity	--	--	--	4225	--	--	6.6230	0.3685	0.0246

N°	Name	T (°C)	P (bar)	m (kg/s)	B_T (kW)	b^{CH} (kJ/kg)	b^{PH} (kJ/kg)	c_T (kJ/kJ)	c_{NR} (kJ/kJ)	c_{CO2} (gCO_2/kJ)
87	Air	25	1	--	--	0.00	0.00	0.0000	0.0000	0.0000
88	Flue Gas	--	1	--	--	--	--	0.0000	0.0000	0.0000
89	Water Losses	25	1	8.2	410	50.00	0.00	0.0000	0.0000	0.0000
90	Condensate	sat	2.5	64.20	7126	50.00	61.00	6.6230	0.3685	0.0246