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Chapter

Aviation Fuels and Biofuels

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Abstract

Aviation industry consumes about 177 billion liters of kerosene, moving more than 25,000 aircraft and 6 billion passengers. To achieve that, civil aviation in 2015 generated about 781 million tons of CO_2 corresponding to 2% anthropogenic emissions of this greenhouse gas, and all required energy is derived from fossil sources. To reduce the environmental impact and to create alternative energy sources to bring energy security, it is of great importance to increase researching and development, so that it becomes viable to produce biokerosene. This chapter aims to present some varieties of biomass and its derivatives being studied as raw materials for new aviation fuels such as ethanol, butanol, fatty acid methyl esters, and fusel oil.

Keywords: biomass, jet fuel, avgas

1. Introduction

Since the beginning of the first civilization, human being has been seeking for progress and better quality of life, developing new technologies and new materials with the aim of making the tasks simpler. The first technology appeared thousands of years ago, using utensils made from chipped stones and evolved in quality and quantity mainly after the industrial revolution in the nineteenth century, to the present day with a great range of consumer goods such as electronics, textiles, automobiles, food, cosmetics, and furniture, among others. To keep and make possible these great advances of mankind, even greater quantities of energy, a essencial necessity, after the industrial revolution had grown rapidly requiring the use of new sources of energy [1, 2].

With the invention of internal combustion engines in the nineteenth century, and the commercialization and popularization of automobiles in the twentieth century, there arose a great and growing need for fuels, which for many years was supplied only with petroleum products, a natural nonrenewable resource. The impacts caused by the oil exploration and the combustion of its derivatives have become serious environmental problems causing a great increase in the emission of greenhouse gases and pollutants, being the main CO_2, SOx, and NOx [3, 4]. Currently, the demand for renewable energy sources is increasing, aiming at reducing anthropogenic CO_2 emissions and reducing society's dependence on oil, and increasing interest in biofuels from biomass.

In the 1970s, Brazil became a pioneer in public policies for the use of biofuels in the energy matrix with the implementation of laws that made mandatory the addition of 10% ethanol in gasoline in 1973 and the launch of the Proálcool program in 1975, which aimed at partial replacement of gasoline by ethanol in the vehicle

fleet, a measure taken in response to the first major oil crisis in the world. The first national biodiesel production program, Pro-Oil, was jointly launched in Brazil, which due to few stimuli for the production of vegetable oils and the fall of oil prices in the 1980s, was unsuccessful, ending in 1986 [5, 6].

The world aviation industry basically uses two types of fuel with distinct characteristics, known as aviation gasoline (AVGAS) and aviation kerosene (QAV) or jet fuel, which consumes around 177 billion liters of fuel worldwide, moving more than 25,000 aircraft. Almost all of this volume comes from petroleum derivatives, a nonrenewable source that handled more than 6 billion passengers [7]. In 2015, civil aviation generated about 781 million tonnes of CO_2 corresponding to 2% of all anthropogenic greenhouse gas emissions according to the Air Transport Action Group (ATAG). Already in 2009, the European Aviation Commission (EAC) determined that emissions from civil aviation should be reduced by 20% by the year 2020, with the use of renewable sources being a highly promising alternative for this goal to be met [8]. Due to the fact that the main oil producers are located in politically unstable countries politically unstable and prices of oil and its derivatives are highly volatile, the need for alternative sources of energy goes beyond the environmental issue.

1.1 Aviation gasoline (AVGAS)

Aviation gasoline known worldwide as AVGAS is a fossil fuel that distills in the range between 30 and 170°C containing gasoline-derived and diesel compounds. This fuel consists mainly of isoparaffins with five to nine carbons, and also, aromatics in small amounts. The main component is alkylate, which is basically a mixture of isooctane (2,2,4-trimethyl pentane) with olefins. Isooctane is a branched chain alkane, octane isomer, which is standard 100 on the octane scale [9].

Aviation gasoline is used exclusively in small airplanes that have spark ignition engines such as aircraft used in agricultural aviation, small commercial aviation, private aviation, pilot training, and in experimental and sporting aircraft. The compound with molecular formula $Pb(C_2H_5)_4$ called tetraethyl lead or TEL is an additive for aviation gasoline that increases the octane rating but it is toxic and releases lead particles into the air [10]. In several parts of the world, this additive is prohibited from being added to the gasoline of land vehicles, however, it is still used in aviation gasoline, with the current technology, it is only possible to achieve an octane rating of more than 100 with the current economic viability through the addition of tetraethyl lead in aviation gasoline in accordance with the standards of the American Society for Testing and Materials—ASTM D3341 or D5059. The most used low lead aviation gasoline is known internationally as AVGAS 100 LL that presents differentiated properties, performance requirements from other gasolines. Throughout the process of handling, transporting, and storing of aviation gasoline, special equipment to the product is used, and the system is periodically inspected to ensure that it is thoroughly clean and free of any possibility of contamination.

The specification of aviation gasoline is practically the same throughout the world, including high calorific value (43.5 MJ kg^{-1}) and low freezing point (−58°C). Constant product monitoring includes daily draining of the storage tank and supply units, filtering of the product prior to filling and periodic inspection of the respective filters. The classification of aviation gasoline is given according to its resistance to detonation in Octane Motor (MON) units according to the ASTM D2700 test. Due to some varieties of aviation gasoline marketed worldwide, the identification of tubing and tanks for refueling was standardized, thus avoiding inadequate fuel supply (**Table 1**).

Type	Color	Lead content (g L^{-1})	Feature
80	Red	0.14	No longer marketed
82 UL	Purple	0.0	Low performance engines
100	Green	1.12	Has been replaced by AVGAS 100 LL
100 LL	Blue	0.56	Worldwide standard

Table 1.
Apparent color and anti-knock power of aviation gasoline [11].
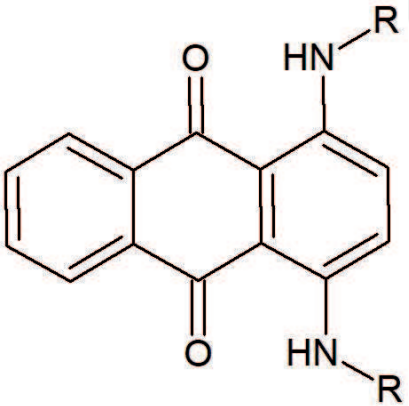
Figure 1.
Blue dye for AVGAS.

AVGAS 100 LL, corresponding to octane 100 and low level of tetraethyl lead is identified with the blue color due to the addition of dye based on 1,4-dialkylamino-anthraquinone (**Figure 1**).

The combustion of a tetraethyl lead fuel generates emissions of both lead and lead oxides, which can accumulate and cause serious damage to the engine. To avoid this accumulation, sequestrants or chelants are used that react with lead compounds and form more volatile species. The most used additives are 1,2-dibromoethane and 1,2-dichloroethane [12]. Despite the significant decrease, it is estimated that the effects of lead to human health cause losses in the US economy of approximately US $ 1.06 billion annually due to public health impacts [13].

The challenges of developing an alternative to lead as an additive in aviation gasoline involve maximum compatibility with existing engines and high reliability. When comparing an airplane engine and a car engine, we have to consider that the operating regime is quite different, in aviation, 80–90% of the time the engine is in high energy demand, and in cars, only 10% on average. Aviation gasoline consists of different types of hydrocarbons that have a higher flash point than that of vehicular gasoline, which starts to release flammable vapor at −42.8°C to optimize its ignition characteristics necessary for the engines [14].

The process of homologation of new additives and fuels is time consuming and costly, especially when compared to vehicular fuels. Despite this, there is not yet an additive that can leave aviation fuels with high octane, since even the use of oxygenated additives have their disadvantages, especially in aviation fuels: increased fuel consumption and increased production of nitrogen oxides.

1.2 Aviation kerosene

Aviation kerosene, also known as jet fuel or by the acronym QAV, is a petroleum source fuel that is in the distillation range between 150 and 300°C and is used in

a medium and large turbine type engine. It is produced by fractionation through distillation at atmospheric pressure, followed by treatments, and is suitable for the generation of energy by combustion in aircraft gas turbine engines. It must remain liquid and homogeneous until the zone of combustion of the aircraft, and have calorific power as high as possible. The specification of aviation kerosene, Jet A-1, is performed in each country to be compatible with the Aviation Fuel Quality Requirements for Operated Systems (AFQRJOS). In order to guarantee the quality of the product until delivery to the final consumer, the Quality Assurance System (QMS) covers the whole distribution chain from the refinery through maritime and land terminals, bases, airport storing, until the supply of the aircraft.

When 1 kg of kerosene is burned, an average of 14 g of NOx; 0.8 g of SOx; 3.15 kg of CO_2; 4 g of CO; and 0.6 g of hydrocarbons are generated, compounds that have a high environmental impact mainly in relation to greenhouse effect and acid rain [15]. In world, commercial aviation is used Jet A1, regulated in Brazil by ANP resolution n ° 37; in the US by the Federal Aviation Administration (FAA) through ASTM D1655 [16, 17]. Jet A kerosene is only used in the USA and differs from Jet A1 at the point of freezing, which is −40°C, higher than −47°C (**Table 2**).

The main fuels used in military aviation are JP-4 and JP-8, with JP-4 kerosene falling out of use since the 1990s due to safety concerns. This fuel is regulated worldwide by the U.S. Military Specification MIL-PRF-5624S and DEF STAN 91-88. JP-8 kerosene is similar to Jet A1 kerosene with the difference of having anti-corrosion additives, dispersants, antifreeze agents, and antioxidants defined by MIL-DTL-83133, DEF STAN 91-87. There is also JP-8 + 100 kerosene containing additives that increase heat resistance at 37°C (100°F) to 218°C over regular JP-8 [18, 19].

In military aviation, there is also kerosene JP5 (European F44), JP7 (US only), JP8 (F34 European), which are chemically similar to the Jet A1 differentiating with respect to antifreeze and antioxidant additives [20] are used. The basic composition of Jet A and Jet A1 kerosene are described in **Table 3**.

In addition to Jet A and Jet A1 kerosene, Jet B type kerosene is the most volatile, thus handling is more dangerous. It has a freezing point below −47°C and is used only in extremely cold regions, such as Canada and Russia. It is mainly composed by hydrocarbons of 5–15 carbon atoms, being actually a mixture of gasoline with kerosene.

In Russia, there is TS-1 kerosene, standardized by the GOST 10227, which differs from Jet A-1 by the freezing point below −57°C and a flash point of 28°C, being lower than 40°C of Jet A1. In addition to Russia, there is also China, which has five

Regulatory agency	Country	Standard/resolution	Jet fuel name
Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP)	Brazil	Resolution n°37	Jet A1
Federal Aviation Administration (FA)	USA	ASTM D1655/ASTM 6615	Jet A e Jet A1/Jet B
Transport Canada Civil Aviation (TCCA)	Canada	CAN/CGSB-3.23 CAN/CGSB-3.22	Jet A/A1/Jet B
Civil Aviation Authority (CAA)	UK	DefStan 91–91	Jet A1
European Aviation Safety Agency (EASA)	EU	AFQRJOS	Jet A1
Federal Air Transport Agency (FATA)	Russia	GOST 10227/GOST R 52050	TS-1/Jet A1
Civil Aviation Administration of China (CAAC)	China	GB 6537	No 3

Table 2.
Main regulatory agencies and technical standards for assessing the quality of civil aviation kerosene in the world.

Compound	Formula	Type
n-Octane	C_8H_{18}	n-paraffin
2-Methylheptane	C_8H_{18}	Isoparaffin
1-Methyl-1-ethylcyclopentane	C_8H_{14}	Cycloparaffin
Ethyl-cyclohexane	C_8H_{16}	Cycloparaffin
o-Xylene	C_8H_{10}	Aromatic
p-Xylene	C_8H_{10}	Aromatic
Cis-Decalin	$C_{10}H_{18}$	Cycloparaffin
Tetralin	$C_{10}H_{12}$	Aromatic
Naftalene	$C_{10}H_8$	Aromatic
n-Dodecane	$C_{12}H_{26}$	n-paraffin
2-Methylundecane	$C_{12}H_{26}$	Isoparaffin
1-Ethylnaftalene	$C_{12}H_{12}$	Aromatic
n-Hexylbenzene	$C_{12}H_{18}$	Aromatic
n-Hexadecane	$C_{16}H_{34}$	n-paraffin
2-Methylpentadecane	$C_{16}H_{34}$	Isoparaffin
n-Decylbenzene	$C_{16}H_{26}$	Aromatic

Table 3.
Jet A and Jet A1 chemical composition [21].

aviation kerosene standards: No. 1 and No. 2, with a flash point near 28°C and freezing point below −60 and −50°C, respectively; No. 3 which is similar to Jet A1; No. 4 which is similar to Jet B; and No. 5 is a kerosene similar to No. 3 but with a high flash point. Currently, practically all kerosene sold in China is No. 3 [22].

The National Agency for Petroleum, Natural Gas and Biofuels—ANP in Brazil, through Resolution 37 of December 2009, specified the technical standard of aviation kerosene, as well as the technical standards for quality control. The quality standards of this resolution are based on the international standards specified in ASTM 1655 and DefStan 91-91. Due to the fact that each country determines its aviation kerosene quality standards, a list of quality requirements for the worldwide commercialization of this fuel, known as Aviation Fuel Quality Requirements for Jointly Operated System (AFQRJOS), has been created. AFQRJOS is based on standards D1655 and DefStan 91-91 and serves as the standard of quality for the main suppliers in the world market as Agip; BP; Chevron Texaco; Exon Mobil; Kuwait Petroleum; Shell; Statoil and Total. For the commercialization of aviation kerosene, rigid physicochemical standards and characteristics are applied, having to deal with approximately 30 tests, a number higher than bioethanol (15 tests) and biodiesel (18 tests).

Aviation kerosene must have a high calorific value (42.8 MJ/kg) coupled with a low specific gravity (0.775–0.820 g mL^{-1}) due to the issue of total aircraft weight, energy efficiency, and flight autonomy [23]. Another important property is the freezing point, due to the working conditions, the fuel should not solidify or form crystals at temperatures below −40°C for Jet A and −47°C for Jet A1 [24]. The moisture content should be low enough to avoid the growth of microorganisms and to reduce corrosivity [25]. The desirable properties of kerosene make the development of biokerosene quite complicated and it is a major obstacle in the search for new alternatives and processes. **Table 4** lists the most commonly used quality technical standards worldwide and the standards in Brazil.

	Unit	ASTM 1655-4a	Def Stan 91-91	ANP n° 37
Density a 15°C	g mL^{-1}	0.775–0.840	0.775–0.840	0.771–0.836* (20°C)
Viscosity a −20°C	mm^2 s^{-1}	8.0 (max)	8.0 (max)	8.0 (max)
Acid value	mg KOH g^{-1}	0.100	0.0012	0.015
Flash point	°C	38 (min)	38 (min)	38 or 40
Heat of combustion	MJ kg^{-1}	42.8 (min)	42.8 (min)	42.8 (min)
Freezing point	°C	−47	−47	−47
Sulfur	%	0.3	0.3	0.3
Aromatics	%	25	25	25
Smoke point	Mm	25 (min)	25 (min)	25
JFTOT Delta P (260°C)	mmHg	25	25	25
Conductivity	pS m^{-1}	50–450	50–600	50–600
Maximum boiling point	°C	300 (max)	300 (max)	300 (max)

Table 4.
Jet A-1 specifications.

Observing ASTM D1655, Def Stan 91-91 and ANP n° 37, it can be concluded that there is a convergence in, practically, all the parameters, differing only in electrical conductivity and acidity. As aviation gasoline, aviation kerosene-containing tubing and refueling tanks are identified by a black color-coded adhesive with an auxiliary color to indicate the type of kerosene (Jet A, Jet A1, or Jet B).

In order to meet the demanding quality parameters of aviation kerosene, compounds known as additives are used, with the objective of improving specific physicochemical properties:

Static charge dissipator: kerosene produced in refineries has low electrical conductivity and this can cause static electricity to accumulate by moving fluid in tanks and filters. To avoid this accumulation a compound known as Stadis 450, which is allowed by ASTM 1655, ANP n ° 37 and DefStan 91-91 in contents up to 5.0 mg/L is added and its use is optional.

Metal deactivator: the presence of metals in the fuel can catalyze oxidation reactions and directly impact thermal stability. The most commonly found metals are Copper and Zinc. The most commonly used additive is N,N-disalicylidene-1,2-propanediamine, which has a chelating action and is used in contents up to 5.7 mg/L [26].

Antioxidants: the formation and presence of peroxides may cause deterioration in the quality of the fuel and may form gums and particulate matter. The use of antioxidant additive is mandatory by ANP n ° 37 and DefStan 91-91 in contents of 17–24 mg L^{-1} and optional by ASTM D1655. The most commonly used compound for this purpose is butylated hydroxytoluene (BHT).

Lubricity enhancer: it has the function of reducing the corrosive effect of the fuel as well as assisting in the anti-wear effect. Its use is not mandatory in kerosene for civil aviation although it is permitted in the Brazilian, US, European Union, and UK legislations and is more commonly used in military fuels (**Figures 2** and **3**).

Icing inhibitors: it is used because of the presence of water in the kerosene, dissolved water can form crystals that can cause clogging of the fuel filter. It is considered optional and is rarely used for civil aviation and most used in military applications and the most commonly used additive is diethylene glycol methyl ether (DiEGME) (**Figure 4**) that may be used as a biocide [27].
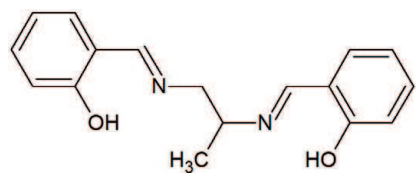
Figure 2.
N,N-*disalicylidene-1,2-propanediamine.*
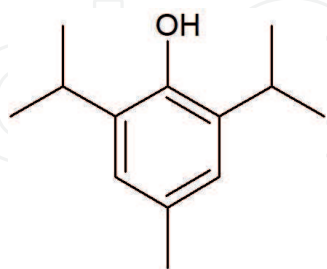
Figure 3.
BHT chemical structure.
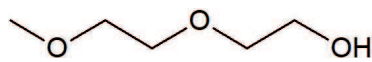
Figure 4.
Diethylene gylcol methyl ether.

Additive type (chemical or brand name)	AFQRJOS Jet A-1	ASTM (Jet A)	DEF STAN 91-91 (Jet A-1)	DEF STAN 91-86 (F-44)	DEF STAN 91-88 (F-40)	IATA (Jet A-1)	CAN-GSB 3.24 (F-34/F-44)	GE D 50TF2	P&W SB, No. 2016
Anti-oxidant	R	O	R	R	R	R	O/R	O	R
2,6-Ditertiary-butyl phenol	●	●	●	●	●	●	●	●	●
2,6-Ditertiary-butyl-2-methyl phenol	●	●	●	●	●	●	●	●	●
2,4-Dimethyl-6-tertiary-butyl phenol	●	●	●	●	●	●	●	●	●
Mix 75%(min) 2,6-ditertiary-butyl phenol	●	●	●	●	●	●	●	●	●
Mix 25%(max) tertiary and tritertiary butyl phenols	●	●	●	●	●	●	●	●	●
Mix 72%(min) 2,4-dimethyl-6-tertiary-butyl phenol	●	●	●	●	●	●	●	●	●
Mix 28%(max) methyl and dimethyl tertiary-butyl phenols	●	●	●	●	●	●	●	●	●

Additive type (chemical or brand name)	AFQRJOS Jet A-1	ASTM (Jet A)	DEF STAN 91-91 (Jet A-1)	DEF STAN 91-86 (F-44)	DEF STAN 91-88 (F-40)	IATA (Jet A-1)	CAN-GSB 3.24 (F-34/F-44)	GE D 50TF2	P&W SB, No. 2016
Mix 55%(min) 2,4-dimethyl-6-tertiary-butyl phenol	●	●	●	●	●	●	●	●	●
15%(min) 2,6-ditertiary-butyl-4-methyl phenol	●	●	●	●	●	●	●	●	●
30%(max) methyl and dimethyl tertiary-butyl phenols	●	●	●	●	●	●	●	●	●
Static dissipator additive	R	O	R		R	R	R	O	R
Stadis 450		●	●		●	●	●	●	●
Sigbol									●
Anti-icing additive	A	A	O	R	R	A	O/A	O	O
Ethylene glycol monomethyl ether							●		●
Ethylene glycol monomethyl ether and Methyl alcohol									●
Diethylene glycol monomethyl ether	●	●	●	●	●	●	●	●	●
Corrosion inhibitors		A	O	R	R	A	A	O	O
Apollo PRI-19		●	●	●	●		●	●	●
Hitec 580		●	●	●	●	●	●	●	●
Nalco 5403		●	●	●	●	●	●	●	●
DCI-4[a]		●	●	●	●	●	●	●	●
DCI-6[a]			●	●	●	●	●	●	●
Nalco 5405						●	●	●	●
Spec-Aid 8Q22						●	●		●
Unicor J						●	●		●
Tolad 351						●	●		●
Tolad 4410			●	●	●	●	●		●
RPS-613						●	●		●
Hitec 515									●
Tolad 245								●	
Mobilad F-800								●	
PWA-536									●
Metal deactivator	O	O	O	O	O	O	O	O	O

Additive type (chemical or brand name)	AFQRJOS Jet A-1	ASTM (Jet A)	DEF STAN 91-91 (Jet A-1)	DEF STAN 91-86 (F-44)	DEF STAN 91-88 (F-40)	IATA (Jet A-1)	CAN-GSB 3.24 (F-34/F-44)	GE D 50TF2	P&W SB, No. 2016
N,N′-Disalicylidene-1,2-propanediamine	●	●	●	●	●	●	●	●	●
N,N′-Disalicylidene-1,2-cyclohexanediamine								●	
Thermal stability additive		A						O	O
Spec-Aid 8Q462								●	●
AeroShell Performance Additive 101								●	●
Turboline FS100C								●	●
Turboline FS100								●	●
JFA-5									●
Leak detection additive		O	O				O	O	O
Tracer A		●	●				●	●	●
Biocide		E			O			O	O
Biobor JF						●		●	●
Kathon FP 1.5						●		●	●

O—Optional: the additive may be added by the fuel manufacturer to the extent permitted by specification without consulting customers. The supplier may be required to declare its presence; A—Agreement: purchasing authorities may require that an additive be used to the extent permitted by specification. If the fuel supplier desires to add it, he must secure agreement of the customer; E—Engine Manufacturer's Agreement: specification authorities may require agreement by engine manufacturers; R—Required: the additive must be introduced at the level specified to meet a specific handling requirement. The point of addition is not necessarily into refinery production (R for anti-oxidant treatment refers to hydrotreated fuel).

Table 5.
Additives for aviation kerosene.

Table 5 lists the main additives required for jet fuel, including the ones mentioned before.

Between 2003 and 2008, the price of aviation kerosene rose 462%, reaching almost US$ 4 per gallon [28] and the economic crisis in 2009 caused a sharp fall reaching close to US$ 1 per gallon. The quotation in October 2016 is US$ 1.47 per gallon [29], data that shows the unpredictability of this input. The Brazilian market follows the external market oscillations, with large variations in the price of this input, which are quite pronounced varying 47% between the years 2008 and 2009, 25% between 2014 and 2016, and comparing 2009–2014, the increase reached 75%. **Table 6** shows the average consumer prices in 11 largest Brazilian capitals between 2008 and 2016.

In the civil aviation industry, the main impact factor in operating costs is the fuel, which corresponds to approximately 40% of the total costs followed by aircraft 20% and operating expenses with 17% (**Table 7**). Therefore, it is extremely important to increase the supply of aviation kerosene, which can be contemplated with new processes and new sources of raw material, and consequently the reduction of its selling price.

Average prices 2008–2016 (without taxes)									
Year	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**
Price (US$/L)	0.44	0.29	0.33	0.41	0.48	0.52	0.54	0.46	0.41

Table 6.
Jet A1 kerosene prices in Brazil between 2008 and 2016 [30].

Category	2009	2010	2011	2012	2013	2014
Crew	12%	12%	13%	11%	10%	10%
Fuel	30%	33%	36%	39%	37%	37%
Depreciation of flight equipment	4%	4%	4%	4%	4%	3%
Aircraft rental, maintenance, and insurance	20%	15%	13%	14%	17%	20%
Airport fees	2%	2%	2%	2%	3%	3%
Air navigation rates	4%	3%	3%	3%	3%	3%
Indirect costs	9%	9%	9%	9%	9%	9%
Operational expenses of public air services	21%	21%	19%	17%	18%	17%

Table 7.
Fight expenses (2009–2014) [31].

2. Biofuels for aviation

The intention of using biofuels in the aviation industry is relatively recent, as research projects have grown significantly after 2010 (**Figure 5**).

Currently, the use of biofuels in aviation suffers from the high production costs that are decreasing and still amount to two to four times the price of fuel of fossil origin, a difference that has already reached 30 times in previous years [33].

During Rio + 20, Azul Linhas Aéreas used sugarcane-derived kerosene supplied by Amyris in an Embraer E-195 for a demonstration flight. Other Brazilian airlines flying with biofuels: GOL Linhas Aéreas, which used biokerosene from corn oil and fry oil in a Boeing 737-800, and LATAM Linhas Aéreas in 2010 using a fuel derived from jatropha oil [34].

Sgouridis and co-workers estimate that 0.5% of the world's jet fuel used in 2009 came from renewable sources and projects, which in 2024, the share will be between 15.5 and 30.5%, depending on public policies and investments and there will be a transport capacity increased by 140% with 20% lower emissions compared to 2004 [35].
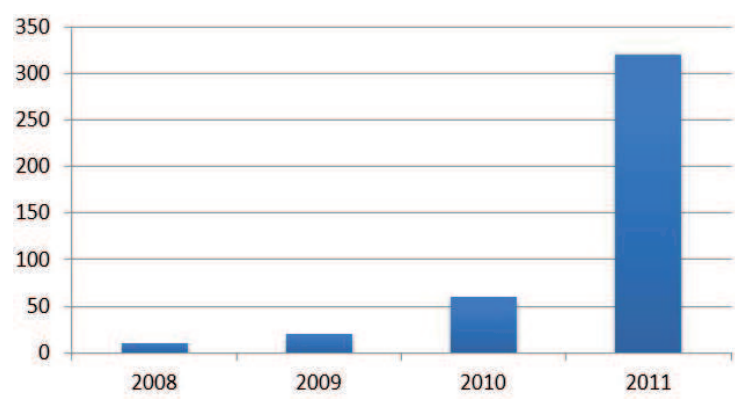
Figure 5.
Number of initiatives for biokeresene production [32].

Production process	Maximum blending
Synthetic paraffinic kerosene (SPK) Hydroprocessed esters and fatty acids (HEFA)	Up to 50%
Synthesized iso-paraffinic (SIP)	Up to 10%

Table 8.
Allowed biokerosene blends [38].

The production of aviation kerosene may be based on the liquefaction and gasification of biomass as well as biomolecules such as alcohols and sugars. The standards DEF STAN 91-91 and ASTM 7566 allow the insertion of paraffins from the Fischer-Tropsch process from renewable sources as semi-synthetic fuel in mixtures of up to 50% with petroleum kerosene.

The Fischer-Tropsch process is based on the conversion of biomass (coal, natural gas, lignocellulosic feedstock, sugars, and vegetable oils) into synthesis gas (syn-gas), consisting of H_2 and CO, which are then polymerized in paraffins, olefins, and compounds carbonylates [36]. Currently, the production of synthetic paraffinic kerosene known as Synthetic Parafinic Kerosene (SPK) is through the use of Fischer-Tropsch (FT) process or hydrotreatment of vegetable oils. We can cite the South African SASOL that produces kerosene from natural gas and coal as well as the North American Syntroleum [37].

In Brazil, ANP resolution n° 63 and in the USA, ASTM D7566 regulates the use of kerosene from biomass with mixtures ranging up to 10% or up to 50%, varying according to the raw material, and the production process (**Table 8**).

2.1 Why use biofuels?

- Reduction of greenhouse gases, mainly the reduced emission of CO_2. Biofuels have a favorable balance of CO_2, depending on the starting biomass and the route used.

- Reduction of atmospheric pollution, such as reduction of SOx, NOx, and CO. The burning of biofuels is generally more efficient and clean than that of petroleum products.

- Increased energy security. The variability of energy sources generates market stability and reduces the risk of scarcity.

- Development of the bioenergy industry, generating jobs, and new possibilities of intellectual capital.

- Decreased dependence on oil, which is a limited natural resource.

We currently have two main bioenergy production chains in Brazil and in the world: the ethanol and biodiesel industry (fatty acid esters). The use and modification has been intensively studied in the partial replacement of both aviation gasoline and aviation kerosene.

2.1.1 Ethanol

The sugar and ethanol industry in Brazil was introduced in the seventeenth century and became one of the main sources of bioenergy inserted in the national energy matrix in the twentieth century. In the 1970s, Brazil became a pioneer in

public policies for the use of biofuels to implement laws that made it mandatory to add 10% ethanol in gasoline in 1973 and the launch of the Próalcool program in 1975 that aimed to partially replace gasoline by ethanol in the vehicle fleet, a measure taken in response to the first major global oil crisis.

According to the Brazilian Ministry of Agriculture, Livestock, and Supply [39], sugarcane production in 2016 was 631.8 million tons and national sugar production was 35.4 million tons, while the ethanol production was 28.526.000 m^3 in that year.

Of this total, 57.1% refers to hydrous ethanol fuel 16.296.000 thousand m^3 [40] and the production of anhydrous ethanol, which is mixed with gasoline A to form gasoline C, recorded an increase of 1.9% in relation to the previous year, totaling 12.230.000 thousand m^3.

Ethanol has been present in civil aviation for more than 10 years with the launch by EMBRAER of the Ipanema agricultural aircraft (EMB-202A) that was designed to be moved to 100% of this biofuel [41]. This aircraft was an adaptation of the aviation-powered gasoline engine (AVGAS 100LL). Two years after the homologation of Ipanema DCTA introduced a flex engine in the T25 model, a less radical and more technologically advanced concept [42].

The use of ethanol replacing aviation gasoline has similar effects to the replacement of vehicular gasoline, such as an increase in average engine power of 7% and a reduction in autonomy of 25–40% due to its lower calorific value (28 MJ kg^{-1} vs. 43.5 MJ kg^{-1}) with higher economic benefits related to the higher cost of aviation gasoline, on average US$ 0.80 per liter, and environmental benefits as a renewable fuel, to reduce CO_2 emissions by up to 63% and with total absence of lead and sulfur [43]. Another advantage that must be mentioned is the tolerance for the presence of water in the fuel, since in airplanes, it is of utmost importance to check the presence of humidity to avoid problems in flight being a standard procedure in this branch of civil aviation.

Due to its large proportions, the sugar and alcohol industry generates several and abundant residues such as vinasse, bagasse, straw, and fusel oil, the last three having an important role in the bioenergy industry and have a great potential for application in civil aviation, either by the use of pure ethanol or by new biofuels developed through this waste.

2.2 Fatty acid methyl esters

Fatty acid methyl esters (FAME) are mainly used as biodiesel, a renewable biofuel obtained through the transesterification reaction of triacylglycerols using methyl alcohol in the presence of a catalyst producing long chain fatty acids esters and glycerin as a co-product (**Figure 6**) [44, 45]. The catalysis used may be acidic, enzymatic, or alkaline, with the most commonly used catalysts being the homogeneous alkalines [46]. These include potassium hydroxide (KOH), sodium hydroxide (NaOH), and sodium methoxide ($CH_3O^-Na^+$).

The main raw materials for the production of fatty acid esters are vegetable oils and animal tallow, which are mainly made up of triacylglycerols. Among the plant sources are the oilseeds, such as the palm (*Elaeis guineensis*), sunflower (*Helianthus annuus*), *Jatropha curcas*, and mainly soybean (*Glycine max*), which corresponds to 68.6% of the Brazilian national production and between animal sources is the bovine tallow with a contribution of 17.3% [47].

Blends of methyl esters of jatropha fatty acids and frying oil have been studied, blends up to 20% v/v with Jet A1 kerosene may be suitable in accordance with ASTM D1655, limited by the fact that these esters have high viscosity (13.02 mm^2 s^{-1} at 50% blend) and also a very far cloud point (−18°C) from desired temperature for Jet A1 kerosene [21].
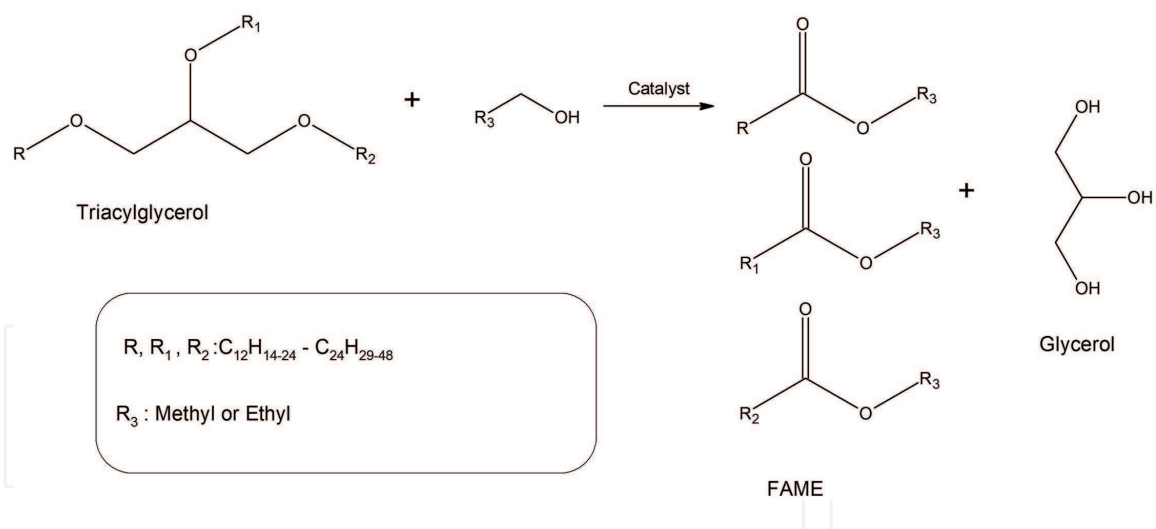
Figure 6.
Transesterification reaction.
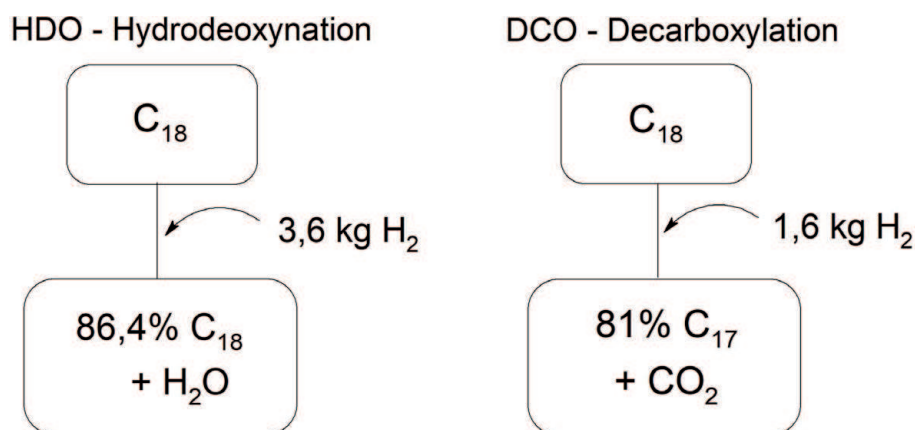
Figure 7.
HEFA for n-paraffin obtention [52].

In addition to conventional sources of fatty acids, we have microalgae, photosynthesizing organisms that have a great potential for lipid production. Studies with *Nannochloris sp., Botryococcus braunii, Chlorella sp.,* and *Scenedesmus sp.* showed great potential for production of lipids and hydrocarbons of high unsaturation, which is unsuitable for application as biodiesel but can serve as an intermediary input in the production of biokerosene [48, 49].

It is considered that the use of fatty acid esters as a partial substitute for Jet A1 kerosene is quite complicated due to very different physicochemical properties, mainly relative to low calorific power, high kinematic viscosity, high metal content, problems with reactions of hydrolysis, and very high freezing point in addition to the possibility of increased oxidative degradation due to the unsaturations of the vegetable oils.

Although their use as esters has not been shown to be consistent, these products open up a great potential as a feedstock for kerosene synthesis by Hydroprocessing of Esters and Fat Acids (HEFA) [50], a route already recognized by ASTM D7566 to be a viable route, mainly due to the great availability and established market [51].

The HEFA process consists basically in the reaction of vegetable oils or biodiesel with hydrogen to remove the carbonyl groups by reducing or forming CO_2, causing loss of a chain carbon, and the formation of n-paraffins, known as Hydrogenated Vegetable Oil (HVO) (**Figure 7**).

The n-paraffins formed in the process have properties suitable for diesel, with high cetane number and high viscosity, which do not yet have properties desired for

Jet A1 kerosene. To improve fuel quality, n-paraffins are subjected to a hydroisomerization (HIS) process for the formation of isoparaffins, a class of compounds highly desired for this purpose.

3. Potential raw materials for aviation biofuels production

As there is an increasing demand for aviation fuels and the difficulties encountered to use methyl esters of fatty acids (FAME), there is a necessity to look for alternative raw materials.

3.1 Fusel oil

Fusel oil is one of the co-products of fermentation for the production of fuel ethanol composed of the less volatile fraction of the distillation [53]. The term "fusel" is derived from German and means "lower"; the composition of that co-product may vary according to the substrate used and fermentative conditions, as well as its yield, which may be 1–11 L for each 1000 L of ethanol produced [53, 54].

The composition of the fusel oil and the contents of the components are shown in **Table 9**.

Table 9 shows two major components together, the isoamyl and isobutyl alcohols (**Figure 8**), contributing up to 65% of the fusel oil according to Pérez et al. [53] and up to 85% according to Patil et al. [55].

The isoamyl alcohol derived from fermentative media is a metabolite generated in the decomposition of an amino acid, isoleucine, mainly by the action of the aminotransferases enzymes and pyruvate decarboxylases, and alternatively

Compound	Content (%)
Isoamyl alcohol	38–85
Isobutyl alcohol	15–20
Methyl alcohol	0.5–2.7
n-Propyl alcohol	0.6–1.4
Ethyl formate	>0.1
2-Butanol	>0.1
Methyl benzoate	>0.1
1-Butanol	>0.2
Hexyl acetate	>0.1
n-Octanol	>0.1
n-Decanol	>0.1
Methyl acetate	>0.1
Amyl acetate	>0.1
3-Pentanol	>0.1
Acetaldehyde	>0.1
Propylaldehyde	>0.01
Amyl alcohol	>0.1

Table 9.
Fusel oil composition.
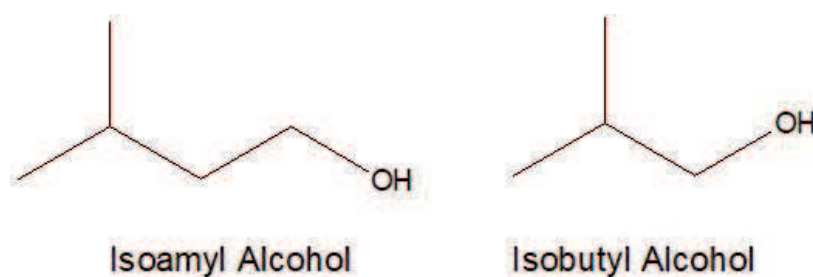
Figure 8.
Representation of the molecular structures of the components with the highest concentration in the fusel oil.

also by routes involving a-ketoacid dehydrogenase and acylCoA hydrolase. In the last decade, fusel oil has been studied for several applications such as synthesis of lubricants by esterification with oleic acid with heavier fractions, obtaining inputs for the pharmaceutical industry, and also in the perfumery industry [56, 57].

Isoamyl alcohol was studied as a total and partial substituent of the vehicle gasoline in 50% fraction, with an increase of up to 25% in the CO emission, with a lower combustion efficiency and a possible shortening of the engine life, indicating that its use as fuel is practically unfeasible in Otto cycle engines [58].

Although its use in pure form is not suitable for use as a fuel, this residue may be a source of branched carbon chain inputs as a starting material for the synthesis of new biofuels as well as for oligomerization reactions in the synthesis of isoparaffins, which are known by producing high-octane fuels to produce kerosene, aviation gasoline, diesel, and lubricating oils with routes similar to those applied to ethanol and n-butanol [59].

3.2 n-Butanol

In contrast to ethanol, n-butanol does not yet have a significant participation in the energy matrix due to its application as a solvent and in the production of resins and to the fact that some countries including Brazil are not self-sufficient in this input. It is considered as a second generation biofuel with higher energy properties and better mixing with paraffinic fuels compared to ethanol.

Butanol can be produced by means of fermentative raw materials of amylaceas and saccharines, obtained by the route acetone-butanol-ethanol (ABE), which is the second most used fermentation process worldwide only losing to the fermentation of ethanol [60, 61]. The most commonly used bacteria for butanol production are *Clostridium acetobutylicum, Clostridium beijerinckii, Clostridium saccharoperbutylacetonicum,* and *Clostridium saccharobutylicum* using various raw materials such as cane molasses, corn husk, cassava flour, bagasse, straw, and sugar cane vinasse [62].

Mixtures of n-butanol and Jet A kerosene were studied and showed a decrease of 5000 rpm in turbine rotation due to its low calorific power (33.08 MJ/kg) compared to Jet A-1 (43.28 MJ/kg), but which had the advantage of significantly reducing NOx and CO emissions by up to 50 and 35%, respectively [63].

Other obstacles in its use are the kinematic viscosity at −20°C of 12.84 $mm^2 s^{-1}$ well above 8.00 $mm^2 s^{-1}$ allowed in the current standards, which can be bypassed in mixtures of up to 20% with Jet A1 kerosene and its high cloud point [64].

The fact that n-butanol has a hydroxyl group makes the fuel more hygroscopic and also denser than a paraffinic kerosene, impairing its energy efficiency. **Figure 9** shows routes for the production of aviation kerosene starting from ethanol and n-butanol known as alcohol to jet (AtJ) [65].
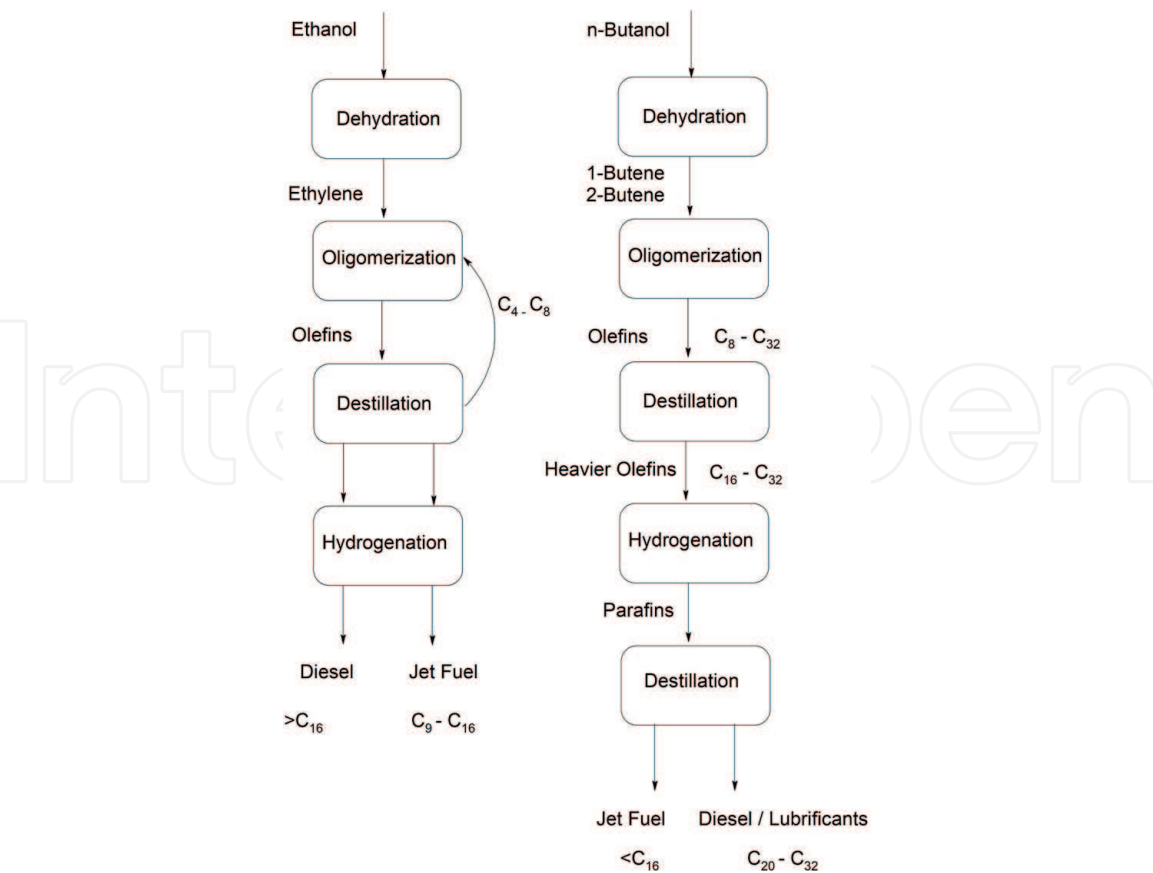
Figure 9.
Routes of obtaining aviation kerosene by alcohol polymerization.

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