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Continuous catalyst free production of biodiesel from agro industrial waste with green solvents

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A mi familia

“La vida no es un problema que tenga que ser resuelto, es una realidad que debe ser experimentada”

Sören Kierkegaard

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Abstract

The aim of this thesis consists in the study of the production of biodiesel via catalyst free direct transesterification of spent coffee ground oil with supercritical methanol in a continuous process. Supercritical methanol is passed through a packed bed reactor with the spent coffee grounds. Inside the reactor supercritical methanol extracts the triacylglycerols, which are immediately transesterified into fatty acid methyl esters. Therefore, the extraction and transesterification processes take in a single step.

It was demonstrated that, at the optimal conditions of operation of 533 K, 10 MPa and solvent flow of 1 ml/min, the maximum yield for the total process was 83%.

The effect of supercritical CO_2 (ScCO2) as co-solvent was also studied. When using carbon dioxide as co-solvent at supercritical conditions, higher yields were obtained at milder temperature conditions. A maximum yield for the total process of 86% was obtained at 314 K for extraction of oil, 473 K for the reaction into FAME, 10MPa, solvent flow of 4.13 ml/min and a volume fraction of $ScCO_2$ in the solvent feed of 27%.

Keywords: Biodiesel; Carbon dioxide; Supercritical fluids; Methanol; Food Industry Waste; Spent Coffee Grounds; Direct Transesterification

Resumo

O interesse de esta tese foi o estudo da produção de biodiesel por transesterificação directa sem catálise do óleo da borra de café com metanol supercrítico num processo continuo. O metanol supercrítico atravessa um reactor de leito fixo carregado com borra de café. No interior do reactor o metanol supercrítico vai extrair os triglycerois, os quais serão imediatamente transesterificados em ácidos gordos metil esterificados. Pelo tanto, o processo de extracção e de transesterificação tem lugar num só passo.

Fica demonstrado que, nas condições óptimas de operação a 533K, 10 MPa e um fluxo volumetrico de solvente de 1 ml/min, o rendimento máximo obtido do processo toatal de extracção de óleo e reacção em metil esteres foi do 83%.

O efeito do CO_2 supercrítico ($ScCO_2$) como co-solvente foi também estudado. Quando o dióxido de carbono é usado como co-solvente nas condições supercríticas, são obtidos maiores rendimentos de metil esteres a umas condições de temperaturas mais reduzidas. Foi obtido um rendimento máximo do processo total do 86% nas condições de temperatura na extracção de óleo de 314 K, temperatura na reacção de FAME de 473 K, 10MPa, fluxo volumétrico de solvente 4.13 ml/min e fracção volumétrica de ScCO2 na alimentação do solvente de 27%.

Palavras-chave: Biodiesel; Dióxido de Carbono; Fluidos Supercríticos; Metanol; Resíduos da Industria Alimentar; Borra de Café; Transesterificação directa

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Abbreviations and symbols

BPR- Back pressure regulator

C16 – Methyl Palmitate

C18 - Methyl Stearate, Methyl Oleate and Methyl Linoleate

CO2 – Carbone dioxide

D – Difusivity

EC- European Commission

EN 14105- European Standard

EU- European Union

FAAE – Fatty Acid Alkyl Esters

FAME – Fatty Acid Methyl Esters

FFA – Free Fatty Acid

GC – Gas Chromatography

K - Kelvin

KOH – Potassium hydroxide

min. – minute

ml- milliliter

MeOH – Methanol

MPa – Mega Pascal

MSW- Municipal solid waste

NaOH – Sodium hydroxide

OECD- Organisation for Economic Co-operation and Development

PC – Critical pressure

PI – Pressure Indicator

TC- Temperature controller

PT-100- Resistance thermometer

SC – Supercritical

scCO2 – Supercritical carbon dioxide;

SCG – Spent Coffee Ground

ScMeOH – Supercritical methanol

TC – Critical temperature

UN- United Nations

wt% - weight percent

ρ – Density

μ- Viscosity

CHAPTER 1: STATE OF THE ART

1.1. WASTE MANAGMENT

1.1.1. An overview

Nowadays the humanity is facing new important challenges; lifestyles and human activities are based in materialism and consume of highly processed goods that are also dependent on energy consumption at a high level. Therefore each year the amount of wastes are increasing and the traditional sources of energy, mainly fossil fuels, are reducing.

There are several factors that point to cause the high levels on waste generation; the increase in world population, high levels of consumption, the increasing wealth of countries and the high technological development. It is anticipated that the combination of these factors could have an impact of a fivefold increase the level of waste by 2025. By 2050 the global population is projected to be 50% larger than today (i.e., 9 billion people), and 95% of that growth is expected to occur in developing countries. [1]

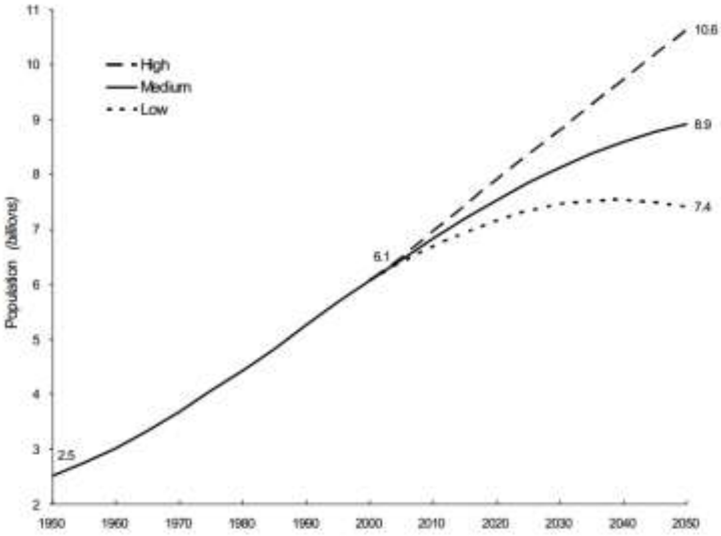


Figure 1.1.1: Estimated World Population, 1950-2000, and projections: 2000-2050. [1]

It is considered a dynamic nature of waste generation process according with three factors: population, technology and affluence, in this way:

Environmental Impact = Population * Technology * Affluence [2]

FACTOR	OBSERVATION
Population	By 2050 the global population is projected to be 50% larger than today (i.e., 9 billion people), and 95% of that growth is expected to occur in developing countries
Consumption	Consumers in certain rapidly expecting non-OECD economies are emulating the ecologically challenging consumption patterns of consumers in OECD countries.
Affluence	Some of the highest GDP growth rates in the world are taking place in countries outside the OECD, such as China, India, Brazil, and Indonesia.
Technology	The Word Bank reports that “massive levels” of industrial investment will occur in developing countries. In principle, “leap-frogging” the dirty technologies of the past may be possible because many developing countries have fewer sunken cost in order to “eco-unfriendly” technologies
Impact	A five-fold increase in global waste generation is possible by 2050

Figure 1.1.2: Dimensions of the waste burden [2]

According to an OECD report data, the highest absolute increase (48%) of waste generation, but lowest relative increase (24%) has been experienced in North America, whereas the lowest absolute increase (34%) has been reported for the European Union countries-but these same countries had the highest relative increase (27%). In the United States the generation per capita of waste is 750 kg, in Japan is 400 kg and in the European Nation the amount varies between 400-800 kg according to the nation [3].

Waste is the result of processes of different activities according to the source community: industrial, domestic, hospital, commercial, agricultural, services and public cleansing. But Industry is by far one that produces greater volumes of waste.

Traditionally the waste treatments technologies were based in common activities like landfill or the incineration, which aim at the elimination of the material. Usually solid waste used to be landfilled, liquid waste going to rivers and seas and gas waste was released into the air. But these applications are not effective enough for the treatment of waste due to the high volumes of material to be processed and their different natures. Moreover, the importance that nowadays there are environmental issues, like climate change. For these reasons, a more sustainable management and use of waste can reduce the potential impact on the human health and environment.

To make a classification of all types of wastes is a difficult task and different authors are not in agreement about that question, but generally, they can be classified based on their source or/and based on their nature. They can also be classified as domestic wastes, commercial wastes, ashes, animal wastes, biomedical wastes, construction wastes, industrial solid wastes, sewer, biodegradable waste, non-biodegradable wastes, and hazardous wastes. [5]

WASTE			
Source	Type	Management Methods	Receiving Medium
Industrial Municipal Animal/ Agricultural Construction Commercial Biomedical	Solid, Liquid, Gaseous Hazardous Toxic Radioactive Biodegradable Non-biodegradable	Incineration Landfilling Recycling Re-using Compost Energy recovery Reduction at source Minimization	Air Water Land

Figure 1.1.3: Waste general characterization

In the “waste puzzle” are included aspects as diverse as the source, the type, the management methods and the receiving medium; the combination of each one of these aspects, determines the kind of residue and the potential solutions that can be implemented in order to minimize its impact in the environment.

Nowadays, the concept of Waste Hierarchy is used as an important tool in the decision making process of waste management. The waste hierarchy favors prevention of waste, followed by reuse, recycling, recovery, with disposal of waste being the last resort.

Figure 1.1.4: Waste hierarchy diagram [3]

However, since different waste treatment methods can have different environmental and health outcomes, it is possible to choose the more appropriate alternative to manage the waste effluent, deviating from the waste hierarchy if justified by life-cycle thinking [3]. The introduction of the concept of 'life-cycle thinking' to waste policy aims at ensuring that the optimal environmental option within the waste hierarchy is selected in each specific situation. The approach examines environmental impacts at each stage in the life-cycle of a resource or a product with the aim of minimizing the overall impacts.

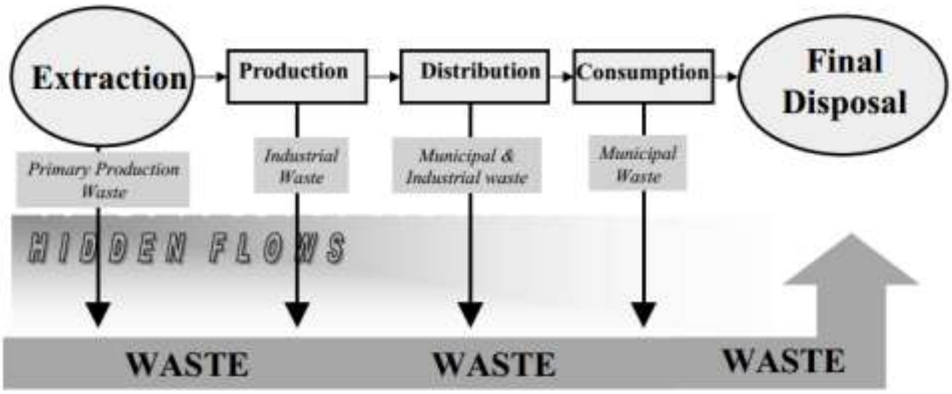


Figure 1.1.5: Life cycle of waste [2]

The Waste Framework Directive (European Commission) also modernized the concept of ‘waste’ to encourage a life cycle approach, for example, by clarifying the distinction between wastes and 'by-products' and introducing ‘end-of-waste criteria' clarifying when waste ceases to be waste [3]. In the other hand, the International Energy Agency provide, within the concept of the life-cycle assessments, the difference between co-products, by-products and waste products; co-products involve similar revenues to the main product, by-products result in smaller revenues, and waste products provide little or no revenue.

There is a widespread interest in treating the waste material so as to produce energy through it in order to encourage different options to the production of alternative sources of energy facing the actual energy crisis. The forms and techniques for it are varied and must be adapted in each type of waste, quality, and local conditions. The main technologies for conversion of solid waste to energy (WTE) are essentially: sanitary landfill, incineration, pyrolysis, gasification, aerobic digestion, pelletization, pyro-plasma and flash pyrolysis. In the figure 1.1.7 is described some of them. These available technologies presents both advantages and disadvantages, thus the best compromise would be to choose the technology, which has lower life cycle cost, needs less land area, causes practically no air land pollution, produces more power with less waste, and causes maximum volume reduction.

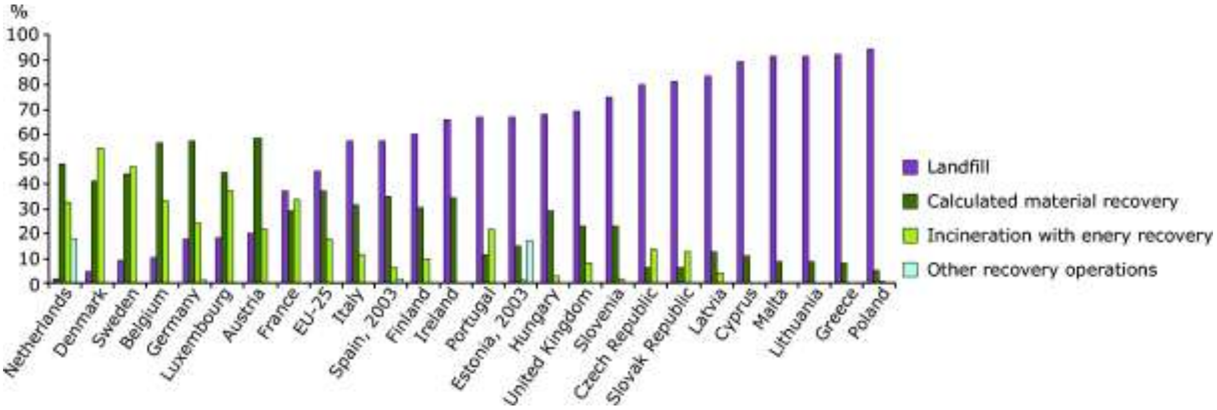


Figure 1.1.6: Recovery operations for waste treatments in European countries [4]

Waste Stream	Waste disposal methods	
Combustible wastes	▪ Roaster incineration ▪ Fluid bed incineration ▪ Pyrolysis – incineration ▪ Pyrolysis – gasification ▪ Separation–composting-incineration ▪ (Wet and dry) separation-digesting-incineration	▪ Separation-digesting-pyrolysis ▪ Separation-digesting-gasification ▪ Separation-digesting-incineration in a cement plant ▪ Selective separation-incineration
Non- combustible wastes	▪ Landfill	
Partially combustible wastes	Wood	▪ Pyrolysis and co-incineration in a coal power plant ▪ Pyrolysis and co-incineration in a powdered coal power plant ▪ Incineration in a fluid bed furnace gasification
	Plastic	▪ Gasification ▪ Feedstock recycling
	Organic wastes	▪ Composting ▪ Anaerobic digestion

Figure 1.1.7: Energy production waste treatment processes [5]

1.1.2. Bio-waste effluents as potential sources of biomass.

The biodegradable wastes refer to the ones that can be decomposed by the natural processes and converted into the elemental form. The principal sources of bio-waste are the agricultural industry and municipal solid waste (MSW). Waste from industrial and municipal sources present an attractive biomass source, as the material has already been collected and can be acquired at a negative cost due to tipping fees [5]. The use of this kind of residue as a source of biomass to generate energy is justified by the fact that the energy content of municipal solid waste (MSW) in the US is typically from 10.5 to 11.5 KJ/kg. Thus bio-waste could be also considered as a relevant source/ type of biomass as it is shown in the figure 1.7. On the other hand the generation and recovery of MSW varies dramatically from country to country. In the the UE-27 annually is between 76.5 to 102 Mt corresponding to the MSW, and 37 Mt of waste from agro-alimentary industry [5]. Is estimated that the Municipal solid waste (MSW) generation has stabilized around 524 kg per year and per capita in 2008 in Europe [6].

Nº	Major Category	Biomass feedstock
1	Forest products	Wood, logging residues, trees, shrubs and wood residues, sawdust, bark, etc.
2	Bio-renewable wastes	Agricultural wastes, mill wood wastes, urban wood wastes, urban organic wastes
3	Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, forage crops
4	Food crops	Residue from grains and oil crops
5	Sugar crops	Sugar cane, sugar beets, molasses, sorghum
6	Landfill	Municipal solid wastes
7	Industrial organic wastes	Plastic wastes, oil wastes, leather wastes, rubber wastes, organic acid wastes, etc
8	Algae, kelps, lichens, and mosses	Water hyacinth, mushrooms, etc
9	Aquatic plants	Algae, water weed, water hyacinth, reed and rushes

Figure 1.1.8: Categorization of biomass stocks [7]

In the European Union waste material generated from manufacturing processes represented 26% of overall waste and Municipal waste represented 15%. According to the European legislation, there is no specific legislation for the management of the alimentary waste, which is a fraction of the Municipal

Solid Waste. They are considered as biodegradable waste or their also called bio-waste, and the treatments for their management are the same for both of them.

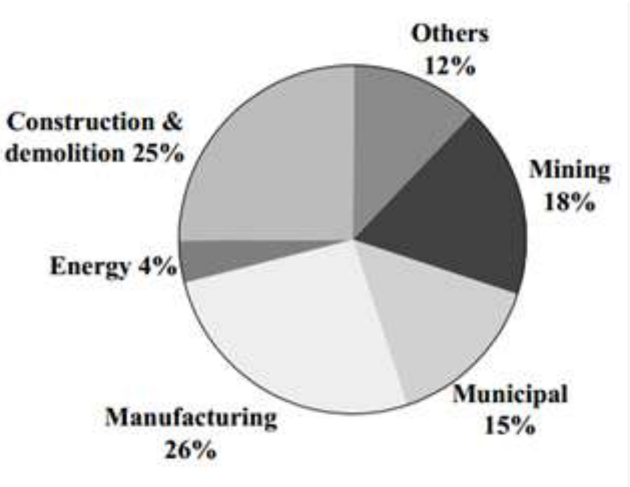


Figure 1.1.9: Approximate waste generation in the European Union by sector [4]

Biomass is the fourth largest source of energy in the world, supplying globally about 10% of primary energy [8] and it is the name given for any organic matter which is derived from plant and animal materials such as wood from forest, crops, seaweed, material left over from agricultural and forestry processes, and organic industrial, human and animal wastes [9]. The two main sources of biomass are the purpose-grown energy crops and wastes. Waste cooking oils [10] animal fats and other biomass residues, like spent coffee grounds, which is a by-product of the existing coffee industry and contains a high percentage of oil [11], are examples for utilizing waste sources for the production of biodiesel. The application of biomass offers many economic advantages like: conservation fuel resources, reduction of the dependence on fuel imports, utilization of agricultural and forest residues, reduction of emission of harmful species from fossil fuel combustion, re-cultivation of non-utilized farming areas, and minimization of waste disposal [12].

There are many different processes to the conversion of biomass, some of them shown in the figure 1.8; direct liquefaction, indirect liquefaction, physical extraction, thermochemical conversion, biochemical conversion, and electrochemical conversion.[13] [14].

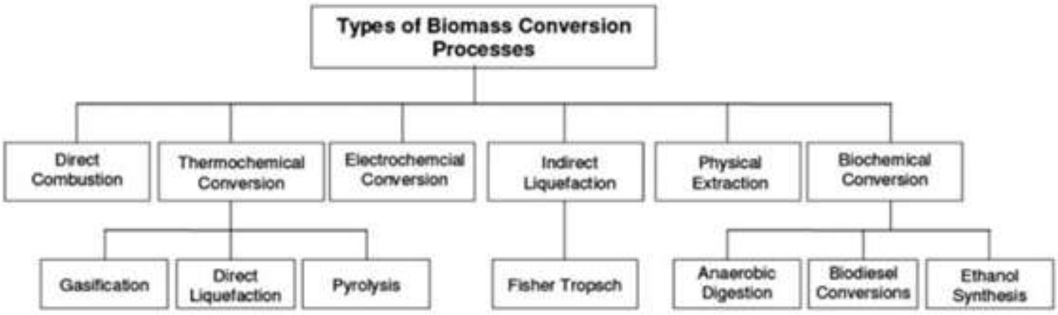


Figure 1.1.10: Classification of biomass conversion processes [9]

The aim of this study is to frame spent coffee grounds (SCG) as a residue with a great potential for energy production amd as a by-product of the industry of coffee instead of a waste with no economic potential associated. Specifically processing this biomass to produce biodiesel with green solvents.

1.1.3. Spent Coffee Grounds as a renewable source

Coffee is one of the most consumed beverages of the world; large quantities of waste generated are a result of the high consumption of coffee worldwide. The mainly producers of coffee in the world are Brazil, Colombia, Vietnam, Ethiopia. The total world production of coffee in the year 2011 was 132,404 million 60-kg bags or 8 million tons. The tree biggest producers of coffee are Brazil, which produced, in 2010, 43,484 million 60-kg bags, Vietnam 18,500 million 60-kg bags and Ethiopia 9,804 million 60-kg bags respectively [15]. Brazil is the world´s largest producer of coffee, representing near the 30% of the global market [16]. *(Production varies significantly from one year to another, e.g. due to climatic conditions)

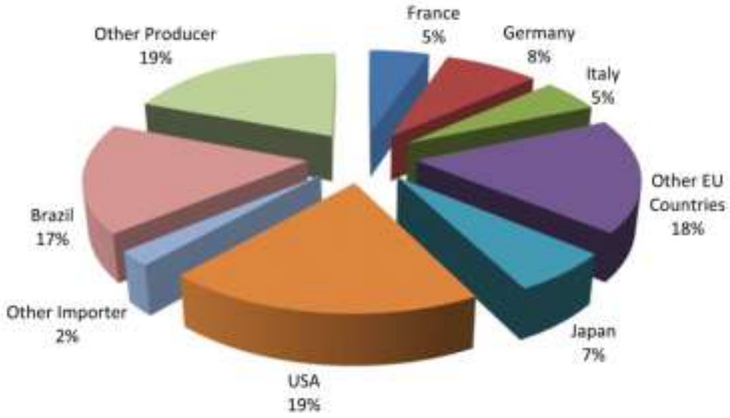


Figure 1.1.11: Worldwide coffee consumption for 2010 [17]

Coffee is the second traded commodity in the world, followed by oil. European Union is the principal coffee imported region in the world with 69 million 60-kg bags per year, followed by USA with 23 million 6-kg bags [17]. Europe produces large amounts of food industrial waste, such spent coffee grounds (SCG), which have largely been under-exploited, most of them with detrimental effects on the environment. SCG are the solid residues obtained from the treatment of coffee powder with hot water to prepare coffee. They are also the main coffee industry residues with a worldwide annual generation of 6 million tons [18].

Chemical composition of Green Coffee, Roasted Coffee and SCG

The composition of coffee is too complex and included more than two hundred substances. The compositions between green coffee beans, roasted coffee and spent coffee grounds are quite different because the variety of the species (*Arabica* or *Robusta*), the roasted process and the method of preparation of the beverage, respectively. The mainly substance present in green coffee beans, roasted coffee and spent coffee grounds are carbohydrates. In green coffee beans the contain of carbohydrates is between 49-64 wt% dry basis, the lipid fraction is mainly composed of triacylglycerols, sterols, tocopherols, and diterpenes of the kaurene family, the latter comprising up to 20% of the total lipids [19]. However, as Lercker et al. [20] had referred, the amount of lipids could increase after the roasted process because the degradation of carbohydrates during the thermic process, also other compounds are modified too. Roasted coffee is composed by carbohydrates (38–42 wt% dry basis), melanoidins (23%), lipids (11–17%), protein (10%), minerals (4.5–4.7%), CGA (2.7–3.1%), aliphatic acids (2.4–2.5%), caffeine (1.3–2.4%), etc.

As Couto *et al.* [21] had reported in SCG, hemicellulose is the mainly compound, 36.7 wt% dry basis. Thus, its indicates that SCG can be used as a source of carbohydrates that can be hydrolyzed to produce reduced sugars, which could be used as carbon sources for several microorganisms. SCG contain on average up to 20 wt% of lipids, 87-93% of them are triglycerides, and 6.5 to 12.5 wt% are diterpene alcohol esters [22]. Triglycerides in the SCG can be converted to a similar amount of biodiesel using the transesterification methods [23]. Lipids tend to concentrate in the spent coffee grounds during the treatment of coffee with hot water or stream, regardless the preparation method used. The fatty acid composition of the oils extracts in the investigations of Couto *et al.* revels that the main fatty acids present in SCG oil are linoleic acid (C18:2) and palmitic acid (C16:0), followed by oleic acid (C18:1) and stearic acid(18:0). Other minors acids present in the extracts are lauric (C12:0), myristic (C14:0), linoleic (C18:3) and arachidic (C20:0) acids.

In general it is considered that the lipid content in the coffee source varies from 10 to 20 wt.% ,in defective coffee beans, the lipid yield ranged from 10% to 12% on a dry weight basis and SCG contain 10-20% wt.%. Assuming 14 wt.% lipid content in SCG, utilizing these lipids for biodiesel and production could add approximately 1123 million tons of biodiesel (based on the year 2010) to the world´s fuel supply [24], Thus coffee oil, extracted from coffee grounds and/or defective coffee beans was found to be a high quality and cost-effective feedstock for biodiesel production compared to other waste sources. It is less expensive, has higher stability (due to its high antioxidant content), and has a pleasant smell [25]. Researchers in USA reported that the resulting coffee based biodiesel is much more stable than traditional biodiesel because of coffee’s high antioxidant content[11]. The remaining solid waste can be utilized as a compost, as a feedstock to produce ethanol and as fuel pellets [11].

Because the importance of the different compounds present in the coffee waste, the extraction of these substances appears as an important alternative to increase the aggregated value of the residue [16]. High added-valued substances in SCG are phenolic compounds, as chlorogenic acids, which presents important antioxidant, anti-bacterial, antiviral, antipertensive, anti-inflamatory and anti-carciogenic activities realted with their antioxidant properties, which make them good compounds for applications in pharmaceutical and food areas [26]. There are other ways of reutilization SCG, outside the field of the energy used, mainly can be used as an antioxidant material source, as it was mentioned before, as a source of polysaccharide with immunostimulatory activity [22] or as adsorbent for the removal of cationic dyes in wastewater treatments [27].

However the main reasons that make SCG a potential source of renewable energy, are large amounts of waste produced, its low toxicity, high calorific power if used as boiler fuel (5000 kcal/kg) [28], no necessity of pre-treatments and a rich source of vegetable oil for biodiesel production. And it is crucial to take into consideration the fact that SCG is also considered an inexpensive and easily available raw material.

1.2. BIODIESEL

1.2.1.Global framework in the emergence of biofuels as an alternative sources of energy

The concept of using biofuels in diesel engines originated with the demonstration of the first diesel engine by the inventor Rudolf Diesel, at the World Exhibition in Paris in 1900, using peanut oil as the fuel. However, due to the then-abundant supply of petroleum diesel at that time, research and development activities on vegetable-oils fuels were not seriously pursued. Nevertheless, today the scenario for the petroleum fuels is changing drastically. Some forecasts indicate that real prices (in 2010 dollars) for motor gasoline and diesel delivered to the transportation sector will increase from $2.76 and $3.00 per gallon, respectively, in 2010 to $4.09 and $4.49 per gallon in 2035. Annual average diesel prices are higher than gasoline prices throughout the projection because of stronger global growth in demand for diesel fuel than for motor gasoline [29].

Figure 1.2.1: Average annual world oil prices in three cases, 1980-2035 (real 2010 dollars per barrel) [29]

Biofuels appear as a solid alternative face to fossil fuels energy crises. Biofuels are liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. They are renewable, sustainable, biodegradable, carbon neutral for the whole life cycle and environmentally friendly. Several biofuels, bioethanol, biomethanol, biodiesel and biohydrogen, appear to be attractive options for the future of transport sector [30].

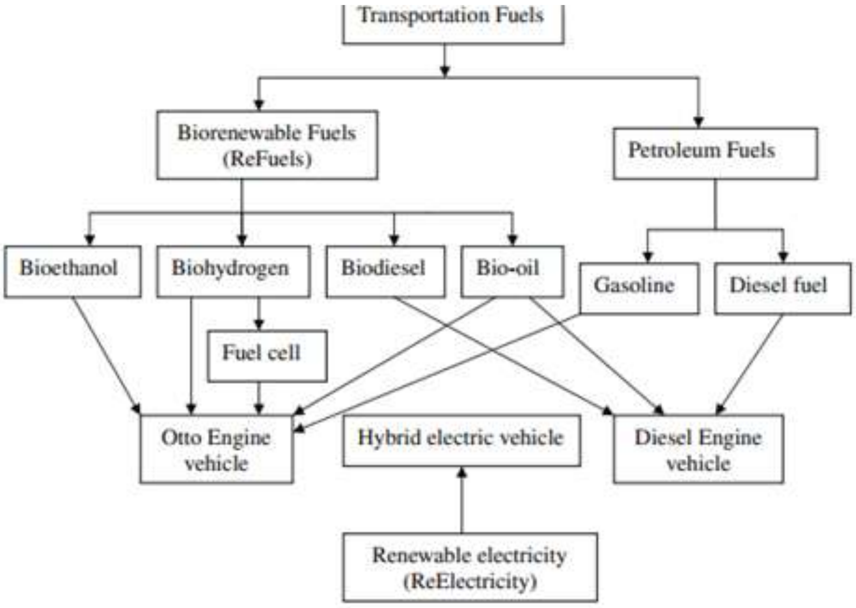


Figure 1.2.2: Transportation fuels and petroleum fuelled, biorenewable fuelled and biorenewable electricity powered vehicle [31]

Biodiesel in particular, represents an the alternative to the conventional fuel for the diesel engine vehicle, which are the main motors used in the transport sector, in Europe.

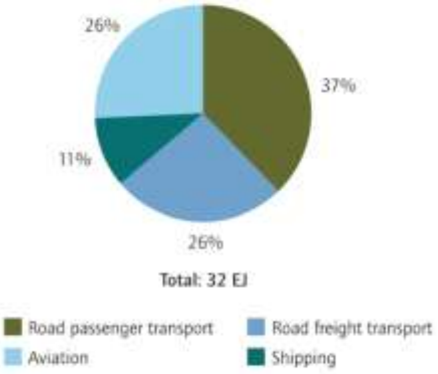


Figure 1.2.3: Use of biofuels in different transport model in 2050 scenario [32]

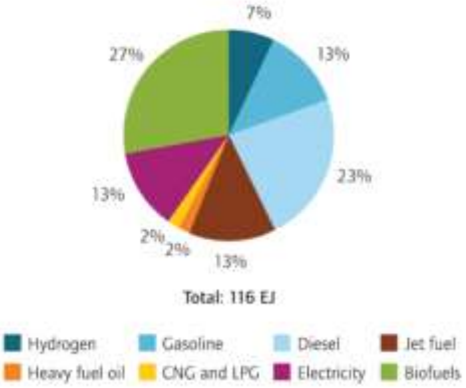


Figure 1.2.4: Global energy use in transport sector in 2050 scenario [32]

The use of vegetable oils as alternative renewable fuel competing with petroleum was proposed in the beginning of 1980s. The advantages of vegetable oils versus diesel fuel are represented as followed [31]:

- Liquid nature-portability
- Ready availability
- Renewability
- Higher heat content (about 88% of no. 2 diesel fuel)
- Lower sulfur content
- Lower aromatic content
- Biodegradability

The disadvantages of vegetable oils as diesel fuel are:

- Higher viscosity
- Lower volatility
- The reactivity of unsaturated hydrocarbon chains

Recently, biodiesel has attracted great attention, due to the awareness of energy supply and the environmental issues associated to fossil fuels. Biodiesel is presented as an sustainable solution because of its renewability, better gas emissivity and biodegradability [10]. Biodiesel is superior to conventional petroleum-based diesel in terms of its sulphur and aromatic content, and flashpoint. However, the high cost of biodiesel compared to petroleum-based diesel, is a major barrier to its commercialization. It costs approximately 1.5 times higher than petroleum-based diesel depending on the sources of feedstock oils [33]. In addition, biodiesel is completely miscible with petroleum diesel fuel and can be employed as a blend [34]

Recently it was reported that about the 85% of the biodiesel production comes from European Union. The demand for biodiesel in European countries was expected to be up to 10.5 billion liters [35].

Country	Production in million liters in 2008
EU 27	9.164
US	3.078
Argentina	1.550
Brazil	1.238
Australia	1.051
Malaysia	609
Indonesia	405
India	227
Canada	114
Other	1.036
World	18.0472

Figure 1.2.5: Production of biodiesel by country in million liters (2008) [36]

1.2.2.Principal Feedstocks and methods for the production of biodiesel

In modern times, biodiesel is derived, or has been reported to be producible from many different sources, including vegetable oils, animal fats, used frying oils, and even soap stock. Generally, factors such as geography, climate, and economics determine which vegetable oil is of greatest interest for potential use in biodiesel fuels. Thus, in the United States soybean oil is considered to be a prime feedstock, in Europe it is rapeseed (canola) oil, and in tropical countries, it is palm oil.[37]. There are more than 350 oil-bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines [38] [39]. Thus nowadays, alternative sources of oil are considered as feedstock, some of them are represented in the figure 1.2.6:

Conventional feedstock		Non-conventional feedstock
Mahua	Soybeans	Lard
Piqui	Rapeseeds	Tallow
Palm	Canola	Poultry fat
Karang	Babassu	Fish oil
Tobacco seed	Brassica carinata	Bacteria
Rubber plant	Brassica napus	Algae
Rice bran	Copra	Fungi
Sesame	Groundnut	Micro algae
Safflower	Cynara cardunculus	Tarpenes
Barley	Cotton seed	Latexes
Laurel	Jatropha nana	
Using cooking oil	Pongamiaglabra	
Coconut		

Figure 1.2.6: Conventional and non-conventional feedstock for biodiesel production [40]

Today, after the controversy over the use of farmland for the production of raw materials for biodiesel versus the use of the land to grow crops for food, actual investigations are more focuses on the search of new sources to produce biodiesel, especially sources based in wastes rich on oil components. Both the second and third generation biofuels are based on the use of raw materials that do not involve season crops.

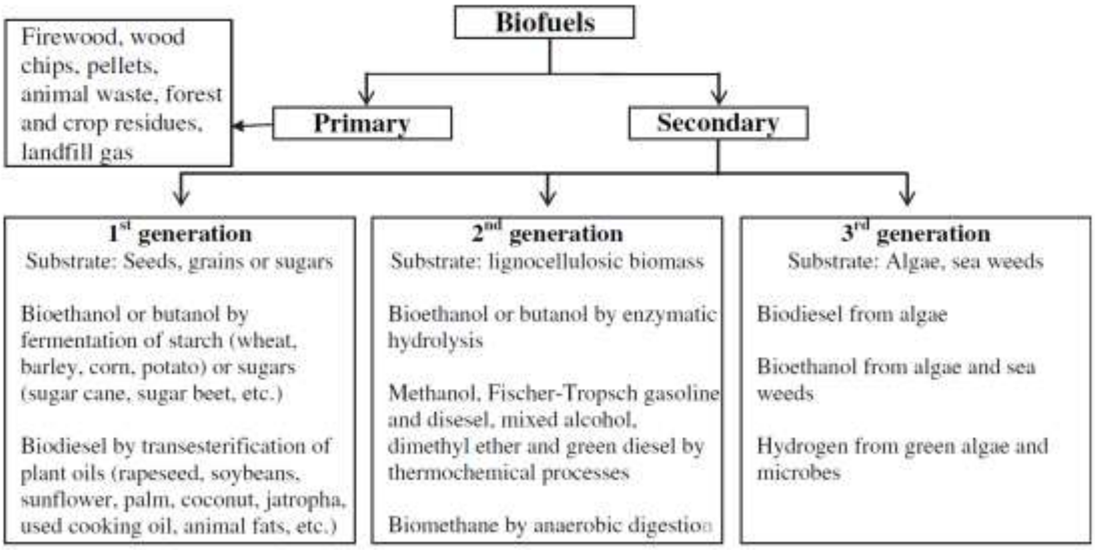


Figure 1.2.7: Production of liquid biofuels from renewable resources [41]

The production of biodiesel and biofuels in general brings an important paradigm shift in terms of production system. Unlike in the case of fossil fuels, where the origin is influenced by the geography and localization of the reserves of the petroleum, the biodiesel production has many different origins in terms of feedstock. Thus, production can be conducted near sources of feedstocks used in each region.

Country	Feedstock
USA	Soybeans/waste oil/peanut
Canada	Rapeseed/animal fat/ soybeans/ yellow grease and tallow/ mustard/ flax
Mexico	Animal fat/ waste oil
Germany	Rapeseed
Italy	Rapeseed/ sunflower
France	Rapeseed/ sunflower
Spain	Linseed oil/ sunflower
Greece	Cottonseed
UK	Rapeseed/ waste cooking oil
Sweden	Rapeseed
Ireland	Frying oil/ animal fats
India	Jatropha/ pongamia pinnata/ soybean/ rapeseed/ sunflower/ peanut
Malaysia	Palm oil
Indonesia	Palm oil/ jatropha/ coconut
Singapore	Palm oil
Thailand	Palm/ jatropha/ coconut
China	Jatropha/ waste cooking oil/ rapeseed
Brazil	Soybeans/ palm oil/ castor/ cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/ tallow

Figure 1.2.8: Current potential feedstocks for biodiesel worldwide [35]

In the manufacturing of biodiesel, fatty acid methyl ester (FAME), from vegetable oil, the level of reaction completion strongly depends on the quality of the feedstock oil [24]. The feedstock represents the mayor problem at the production of biodiesel process today, as figure 1.2.10 shows. One problem associated with that issue is the fact that with the increase in global human population, more land will be needed to produce food for human consumption. Thus, the insufficient lands could increase the cost of the feedstock and consequently biodiesel production. Therefore, other alternative feedstock are widely investigated and are new technologies are been developed in order to achieve a less expensive production of biodiesel. For instance, non-edible oil, genetically engineered plants, microalgae, wastes feedstocks can be proper solutions for this problem and can ensure the sustainability of biodiesel production in the future [35].

Feedstocks	Oil content (%)	Oil yield (L/ha/year)
Castor	53	1413
Jatropha	Seed: 35-40 Kernel: 50-60	1892
Linseed	40-44	-
Soybean	15-20	446
Sunflower	25-35	952
Rapeseed	38-46	1190
Palm oil	30-60	5950
Peanut oil	45-55	1059
Olive oil	45-70	1212
Corn	48	172
Coconut	63-65	2689
Cottonseed	18-25	325
Rice bran	15-23	828
Microalgae (low oil content)	30	58,700
Microalgae (medium oil content)	50	97,800
Microalgae (high oil content)	70	136,900

Figure 1.2.9: Estimated oil content and yields of different biodiesel feedstocks [35]

As it has shown in the figure 1.2.10, the production process, itself, adds only about 5–30% to the production costs of biodiesel. The best chance to reduce production costs lies in minimizing the cost for the input material [42]. It is reported that approximately 70-95% of the total biodiesel production cost arises from the cost of raw materials.

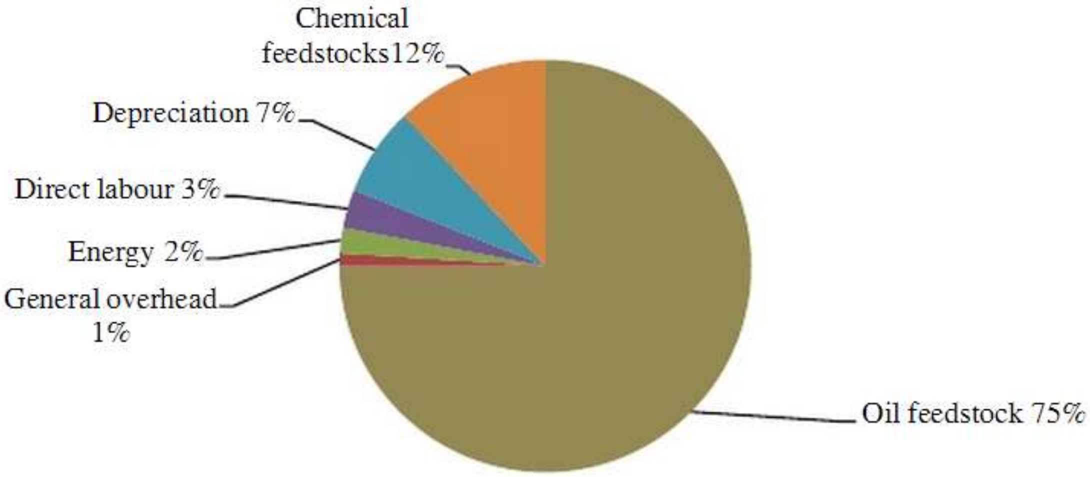


Figure 1.2.10: General cost breakdown for production of biodiesel [35]

The major problem associated with the use of pure vegetable oils as fuels, for diesel engines are caused by high fuel viscosity in compression ignition.[43]. Thus direct use in compression ignition engines was restricted due to high viscosity which resulted in poor fuel atomization, incomplete combustion and carbon deposition on the injector and the valve seats causing serious engine fouling [44]. Due to their high viscosity (about 11–17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Other constraints of the direct application of vegetable oil were its low volatility and polyunsaturated character. To overcome these constraints, some processes were especially developed :

- Dilution of 25 parts of vegetable oil with 75 parts of diesel fuel,
- Microemulsions with short chain alcohols such as ethanol or methanol,
- Thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds,
- Catalytic cracking, which produces alkanes,cycloalkanes and alkylbenzenes, and
- Transesterification with ethanol or metanol

Technologies	Advantages	Disadvantages
Dilution (direst blending or micro-emulsion)	• Simple process	• High viscosity • Bad volatility • Bad stability
Pyrolysis	• Simple process • No- pollution	• High temperature required • Equipment is expensive • Low purity
Transesterification	• Fuel properties is closer to diesel • High conversion efficiency • Low cost • It is suitable for industrialized production	• Low free fatty acid and water content are required (for base catalyst) • Pollutants will be produced because products must be neutralized and washed • Accompanied by side reactions • Difficult reaction products separation
Transesterification in Supercritical methanol	• No catalyst • Short reaction time • High conversion • Good adaptability	• High temperature and pressure are required • Equipment cost is high • High energy consumption

Figure 1.2.11: Comparison of main biodiesel production technologies [45]

The transesterification, reaction of triglycerides with short-chains alcohols, seems to be the best choice, as the physical characteristics of the product, fatty acid esters (biodiesel), are very close to those of diesel fuel, and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.[43].

Vegetable oils can be transesterified by heating them with a large excess of anhydrous sort chain alcohol, e.g., methanol or ethanol, with or without the present of a catalyst. The reaction can be catalyzed by alkalis, acids, or enzymes [46]. Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in general, a higher molar ratio is often employed for maximum ester production yield.

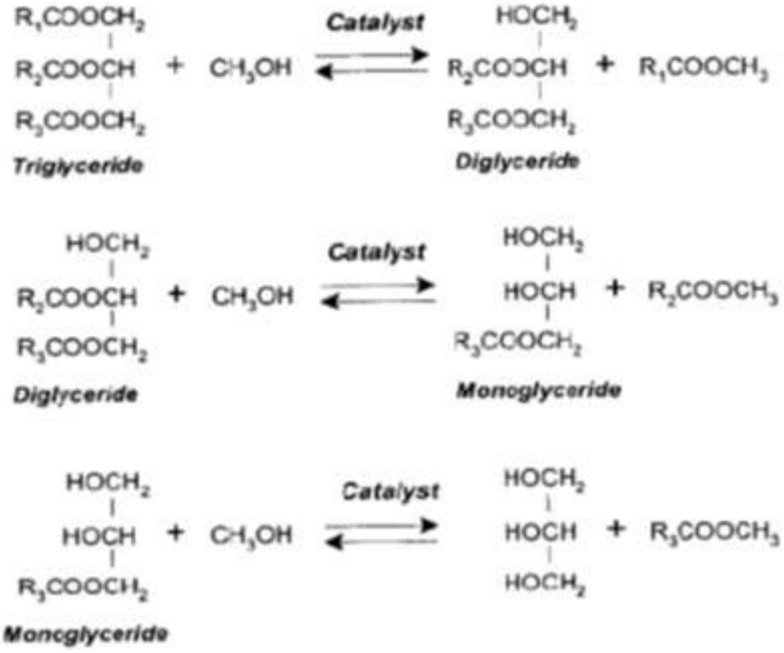


Figure 1.2.12: Intermediate steps in tranesterification reaction

The overall reaction kinetics is dependent on the individual rate constants for the conversion of triglycerides to diglycerides, monoglycerides and alcohol esters. Diverse authors in the literature consider a first order reaction , and they consider, as well, the reaction irreversible [47].

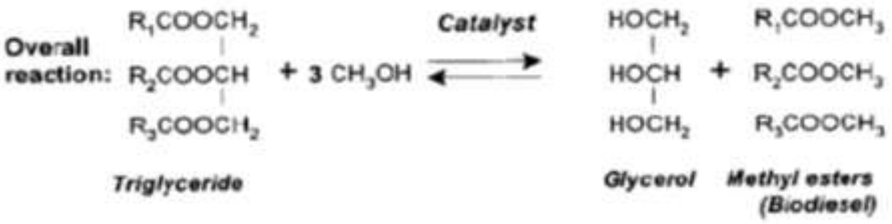


Figure 1.2.13: Overall tranesterification reaction [48]

Commonly used alcohols include methanol, ethanol, propanol and butanol. The selection of one alcohol depends on cost and its performance in the reaction. Even though ethanol represents a renewable source, methanol is preferred over others due to its low cost, simplicity of the process with lower reaction time, spontaneous separation between glycerol and methyl esters and high reaction yield.[37]

Product	Production process
Methanol	Distillation of liquid from wood pyrolysis Gaseous products from biomass gasification Synthetic gas from biomass and coal Natural gas Petroleum gas
Ethanol	Fermentation of sugars and starches Bioconversion of cellulosic biomass Hydration of alkanes Synthesis from petroleum Synthesis from coal Enzymatic conversion of synthetic gas

Figure 1.2.14: Main production facilities of methanol and ethanol [44]

In figure 1.2.14 are indicated the actuals methods of production biodiesel via tranesterification reaction, some of them, like homogeneous catalytic methods, are commercially used in today’s industrial process and others are still under investigation, like supercritical method.

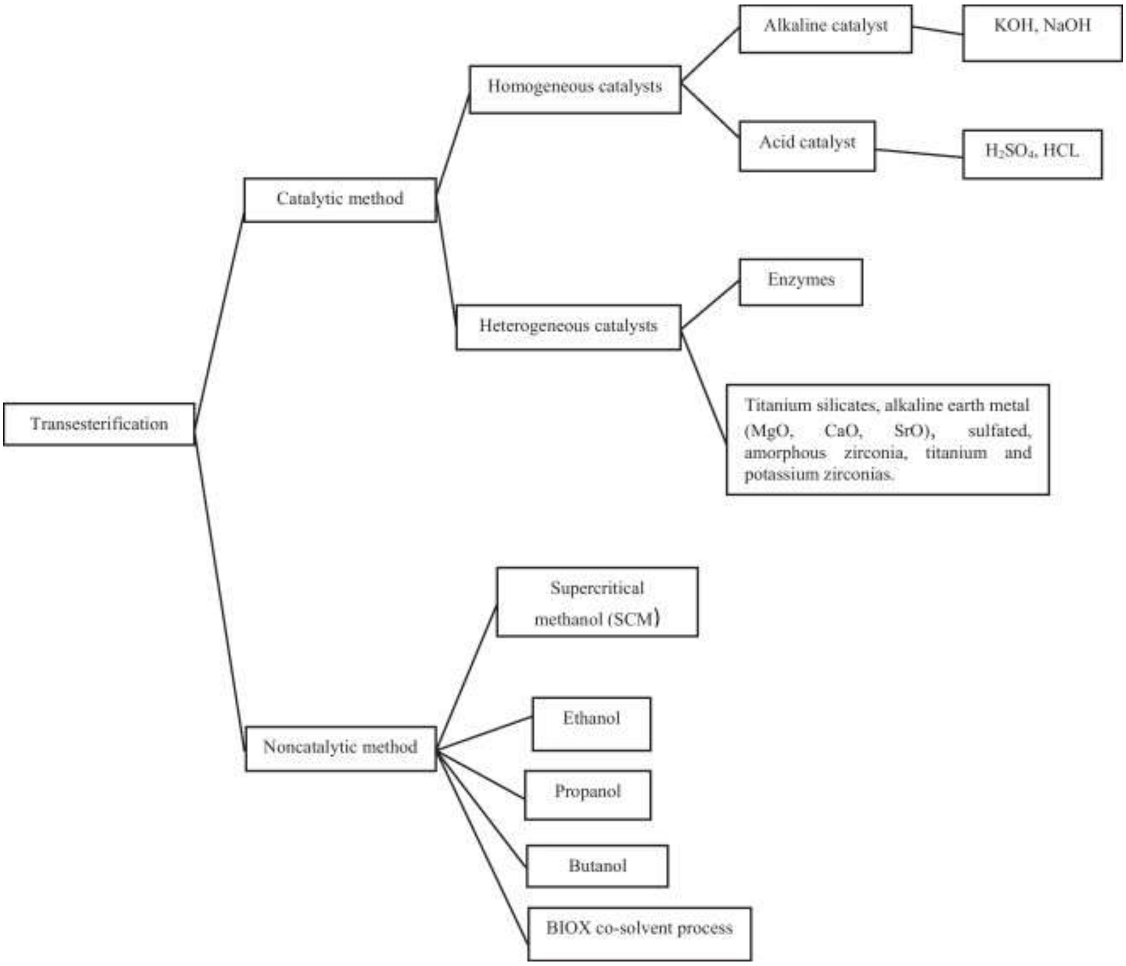


Figure 1.2.15: Classification of transesterification processes [35]

Nowadays and in high scale production, common process to produce biodiesel is by catalyst transesterification methods, mainly using basic catalyst as KOH or NaOH. The alkali-catalyzed transesterifications is much faster than the acid-catalyzed transesterification In both cases the transesterification reaction is initially slow because of the two-phase nature of the alcohol/oil system, and slows even further because of polarity problems [48] . However, non-catalytic methods are widely investigated due their advantages in terms of time reaction, low amount of equipment required, no purification process of impurities and high yield achieved.

The parameters that usually effect the tranesterification reaction are:

- moisture and water content
- molar ratio of alcohol:oil
- catalyst type
- type of alcohol used

- temperature
- pressure
- free fatty content [46].

In conventional catalyst tranesterification, water and free fatty acids content are an important factors, and always produce negative effects, since the presence of free fatty acids and water causes soap formation, consumes catalyst and reduces catalyst effectiveness, all of which results in a low conversion [46]. On the other hand these aspects present no relevance in the case of the supercritical tranesterification method. The next figure are represented the advantages and disadvantages of the actual transesterification process

Variable	**Base catalyst**	**Acid catalyst**	**Enzyme**	**Supercritical alcohol**
Temperature (ºC)	60-70	50-80	30-50	200-350
Products from FFA	Soaps	Esters	Esters	Esters
Effect of water	Negative	Non effect	Negative	No effect
Yield to ester	Normal	Normal	High	High
Purification of glycerol	Difficult	Difficult	Simple	Simple
Reaction time	1-2 h	4-70 h	8-70h	4-15 min
Ester purification	Difficult	Difficult	Simple	Simple
Cost	Cheapest	Cheapest	Expensive	Expensive
Amount of equipment	High	High	Low	Low

Figure 1.2.16: Comparison between different technologies in tranesterification for biodiesel production [49]

1.2.3. Future trends and outlook

The actual concerning in the research and production of biofuels technology today is not only orientated because as a result of a green sentiment , it is also arises due to insecurity in terms of energy that many nations all over the world fell nowadays in terms of energy capacity and resources. In that frame, the production of biofuels is expected to rise steadily in the next few decades. The global biofuel production is estimated to reach 1,900 Million barrel in 2020, at a compound annual growth rate of 10% over the forecast period 2015–2020 [50]

They are describing in the figure 1.2.16 some critical components that should be in place for the biofuels market to happen today.

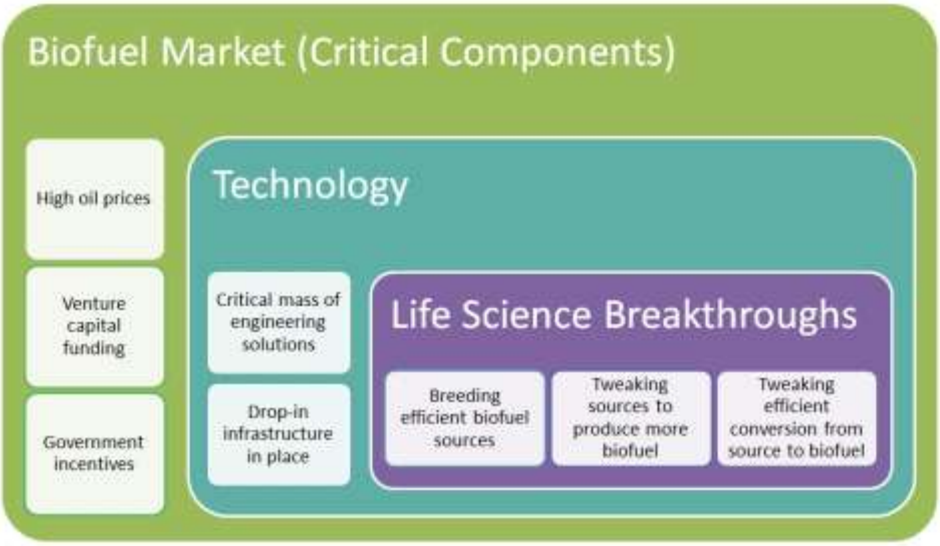


Figure 1..2.17: Critical components within market, technology and life science frameworks in the biodiesel market [50]

Today biofuels represent an emerging market, where countries like Brazil, the United States, Canada, Europe, Australia, India, China, Japan, Malaysia, and Thailand are presented as main producers. It is expected that in the future this trend will grow and new countries join the development of biofuels [51], [52]. Many of them have biofuels policies in place or in formulation. REN21, the Renewable Energy Policy Network for the 21st Century, reported 73 countries (many of them developing countries) as bioenergy targets from early 2009 [53]. In the United States the Renewable Fuels standard (RFS 2) lays out the strategy and targets for the US to 2022. The goal is to use at least 36 billion gallons of bio-based transport fuels by 2022 [54]. It is estimated that biodiesel can replace approximately 10% of total diesel consumptions in Europe and 5% in Southeast Asia [55]. In the European Union, the world’s largest biodiesel producer, biofuel consumption is mostly driven by mandates in both France and Germany [55] that sets a minimum mandatory percentage of biodiesel to be blend with commercial diesel . It is anticipated that the European policy will lead to a total bio-fuel demand in EU of around 30.3 MTon by 2020 [33].

The market for biofuels is still in an early and very dynamic stage [30]. Production in general is unprofitable and it needs to be promoted via tax exemptions, subsides or other forms of financial incentives.

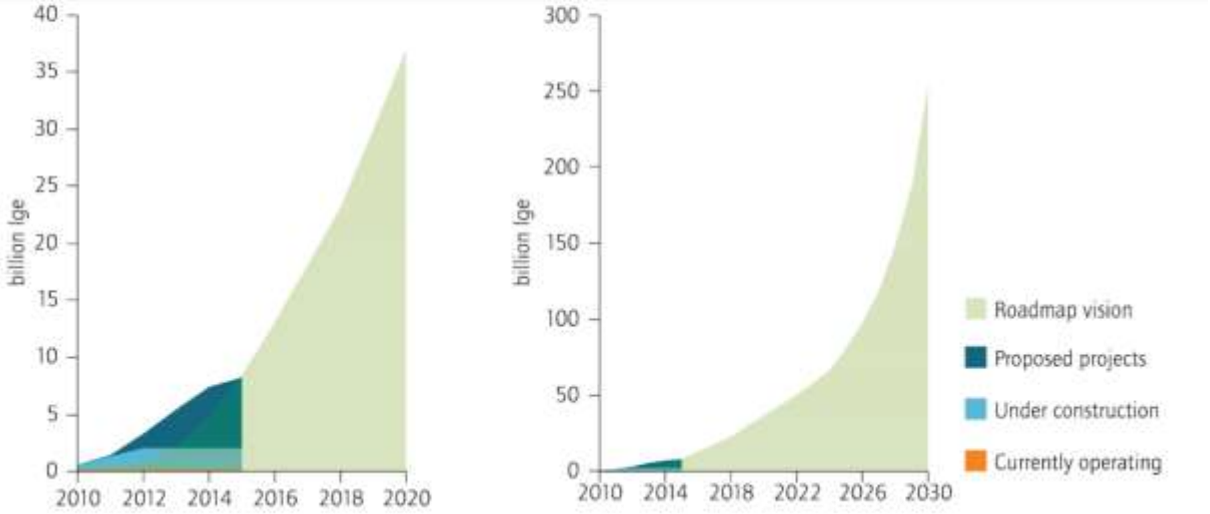


Figure 1.2.18: Advanced biofuel production capacity to 2015, 2020, 2030 [32]

Today the most important issues that are based on the sustainability of biofuels as an alternative energy are based on social, economic and environmental aspects. The set of all, help to enliven the biofuels market in the coming years face to the crisis of the fossil fuel market. As has been pointed in a recent report about biofuels in Europe, the new generation of biofuels and biodiesel as well, brings a new sustainable business model (figure 1.2.18). In that new scenario, most of the second and third-generation biofuels will be derived from perennial plants, wastes sources or microalgae production, but achieving that diversity is likely to depend on greater investment in biofuels R&D and demonstration plants.

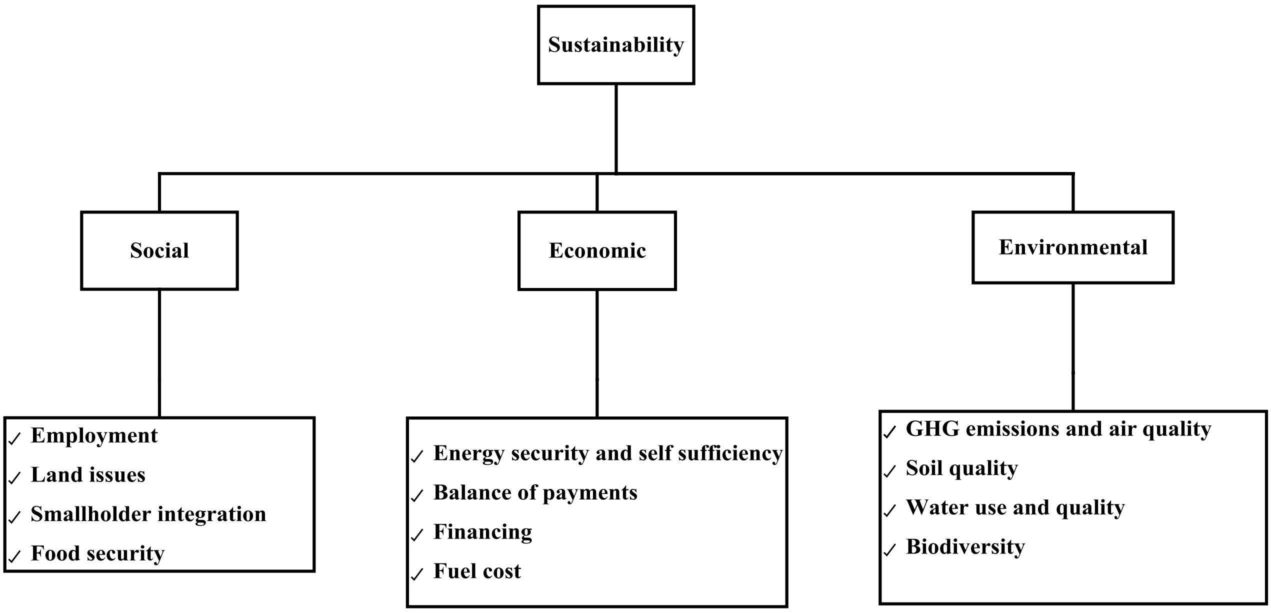


Figure 1.2.19: Environmental, social and economic aspects of biofuel and bioenergy production [32]

1.3. SUPERCRITICAL FLUIDS

Supercritical fluids (SCFs) are substances at pressures and temperatures above their critical values. A pure component is considered to be supercritical if its temperature and pressure are higher than the critical values (T_c and p_c, respectively). Above critical conditions for pressure and temperature, there is no sudden change of component properties. The variation of properties with conditions of state are monotonous, when crossing critical conditions [56].

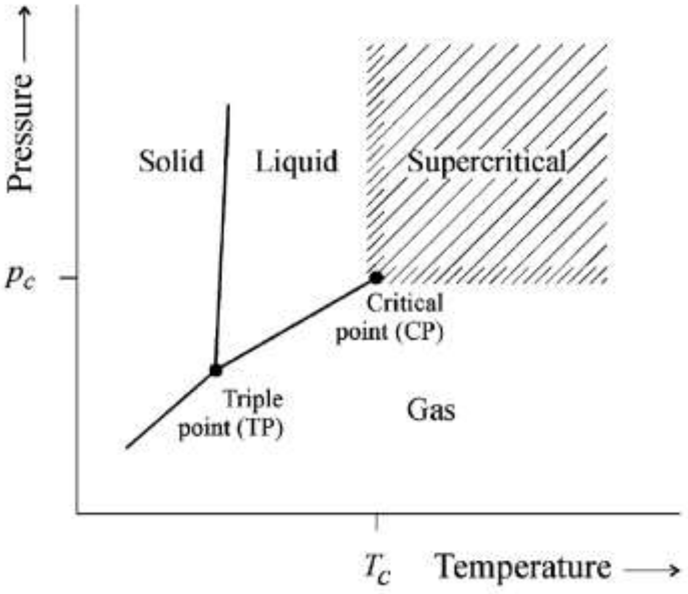


Figure 1.3.1: General diagram of supercritical state for a pure component [56]

At the critical point, the densities of the liquid and gas phases become identical; the distinction between the gas and the liquid disappears. The substance is now described as supercritical fluid. The critical point has pressure and temperature co-ordinates on the phase diagram, which are referred to as the critical temperature, $T_{c,}$ and the critical pressure, P_c, and which have particular values for particular substances [57].

1.3.1. Characteristics of SCF

The principal properties of the supercritical fluids are mainly their density, viscosity, diffusivity and solvent strength. In the supercritical region, liquid-like densities are approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical liquids, as it is showed in figure 1.3.2 [56].

	Density (kg/m^3)	**Viscosity (mPa*s)**	**Diffusivity (cm^2/s)**
Gases	1	0.01	0.1
SCFs	500	0.1	0.001
Liquids	1000	1	0.0001

Figure 1.3.2: Properties of supercritical fluids

Two different effects are present in the SCF properties:

- Solvent power of a SCF increases with increasing density
- Vapor pressure of a solute increases exponentially with the temperature

Solubility of a low volatile component, as triglyceride, in a supercritical solvent, such as methanol or methanol/CO_2 mixtures, exhibits a characteristic scheme: at high pressures solubility increases with temperature and at low pressures solubility decreases with temperature, this is illustrated in the figure 1.3.3:

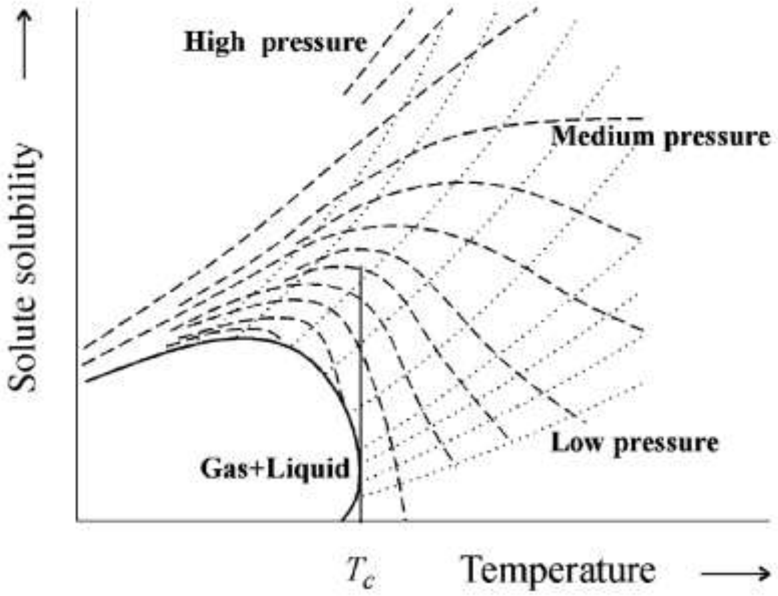


Figure 1.3.3: Variations in the solubility of a low-volatility substance [58]

Properties of the solvents, in the critical area, like temperature and pressure are different from those of a solvent in the liquid or gaseous state far from the critical temperature. In the critical region, properties vary very drastically within narrow ranges of pressures and temperatures, thus producing quite different affects at neighboring conditions of state [58]

A fluid should have some important characteristics to be practical in terms of industrial application. These are:

- ✓ Inexpensive (< 0.15 €/ Kg ideally)
- ✓ Non toxic
- ✓ Non flammable
- ✓ Commercially available
- ✓ Easy purification
- ✓ p_c, T_c near ambient conditions
- ✓ Good solvent properties
- ✓ Co-solvents may be useful (MeOH, Acetone, ect)

Table 1.3.1: Critical properties of some fluids [59]

Solvents	Critical Temperature (°C)	Critical Pressure (bar)
Carbon Dioxide	31.1	73.8
Nitrous Oxide	36.5	71.0
Ethane	32.2	48.8
Ethylene	9.3	50.4
Propane	96.7	42.5
Propylene	91.9	46.2
Cyclohexane	280.3	40.7
Isopropanol	235.2	47.6
Benzene	298.0	48.9
Toluene	318.6	41.1
p-Xylene	343.1	35.2
Chlorotrifluoromethane	28.9	39.2
Trichlorofuoromethane	198.1	44.1
Ammonia	132.5	112.8
Water	374.2	220.5

Usually CO_2, propane, butane, 134a, are good choices as fluids to work with. Water and carbon dioxide, especially in their supercritical region, are primary candidates as solvents for green chemical process, since they are compatible with the environment and have enhanced transport properties for reactions and separations. The principle problem to work with supercritical water is the corrosion [60]. Nitrous dioxide was used in the past due to its best solvent power than carbon dioxide, but nowadays its use has been abandoned as it may lead to oxidation and explosive reactions.

1.3.2.Advantages and disadvantages of the SCF technology

Supercritical technology is taking more and more attention today because it is a clean and environmental friend technology. One of the principal advantages of using SCFs is the possibility to operate in a large scale of conditions in the same process in order to obtain different products,. This can be achieve by applying small changes in temperature and pressure condition, and therefore altering the solvent power of the supercritical fluid. Different outcomes can be achieved using the same equipment without additional cost. This shows that it is a highly versatile technology.

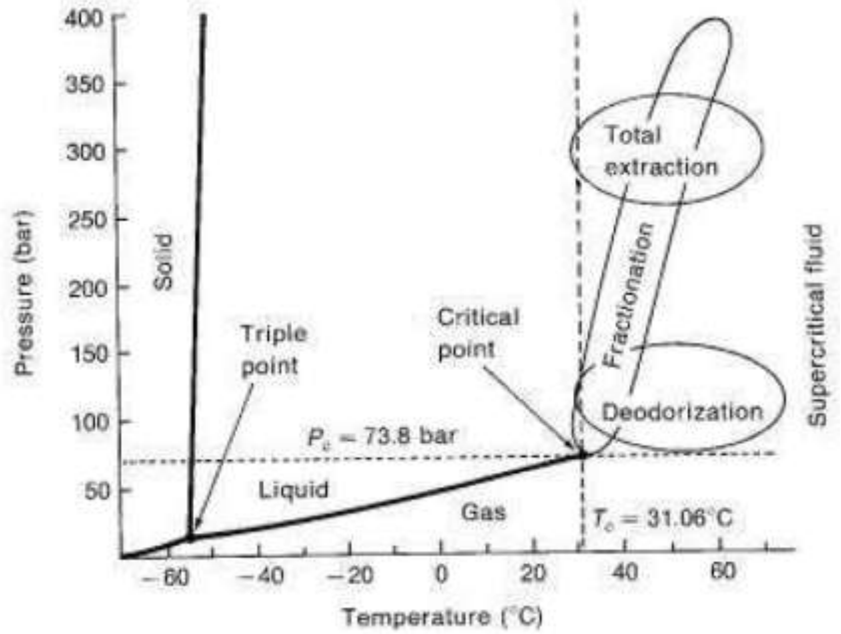


Figure 1.3.4: Change solvent capacity of a fluid at different pressures [59]

On the other hand, the principal disadvantages of the use of supercritical fluids are the large amounts of energy required in order to achieve the necessary operation conditions, usually high temperature and pressure, as well as the elevated cost of the specific equipment that the high pressure technology requires. The additions of co-solvents are presented as an alternative to reduce the side effects that cause the aggressive conditions of the processes in the equipment and more important, to reduce the conditions in pressure and temperature of the main fluid at supercritical conditions, reducing as well the amount of energy required. It is also have to take under consideration the fact that if it´s chosen, there are important mechanical issues associated with high pressure technology to face in a project using SCF.

In conclusion a SCF will be used in a process in the cases where the product has a high added-value associated; when the SCF process gives superior product properties than conventional process; when a strictly solvent-free product is required; in cases of environmental, health or energy reasons. SCF process is also appropriate when the controlling mass transfer resistance is much lower than in the conventional process.

1.3.3.Applications of SFC technology

Today the organic solvents represent a serious threat to the environment; they are used in a wide scale by a diverse range of global industry in many process. Actual tendency is to make the industry adopts more environmental friendly process. To make chemical processes more environmentally friendly and reducing the amount of hazardous wastes, solvent substitution was proposed in the1990 decade. Especially the use of SCF technology is emerging as an important alternative to this issue, between other methods like the use of aqueous solutions, ionic liquids, immobilized solvents, solvent free conditions, low-toxicity organic solvent, and fluorous solvents [60].

Interest in supercritical fluids owing to their properties and relatively low environmental impact. Greatest attention has been given to the extraction and separation of organic compounds. Supercritical fluids have also been successfully used for particle production, as reaction media, for the destruction of toxic waste. Supercritical fluids have also been used on analytical and preparative scales for many biological and other applications. [57]

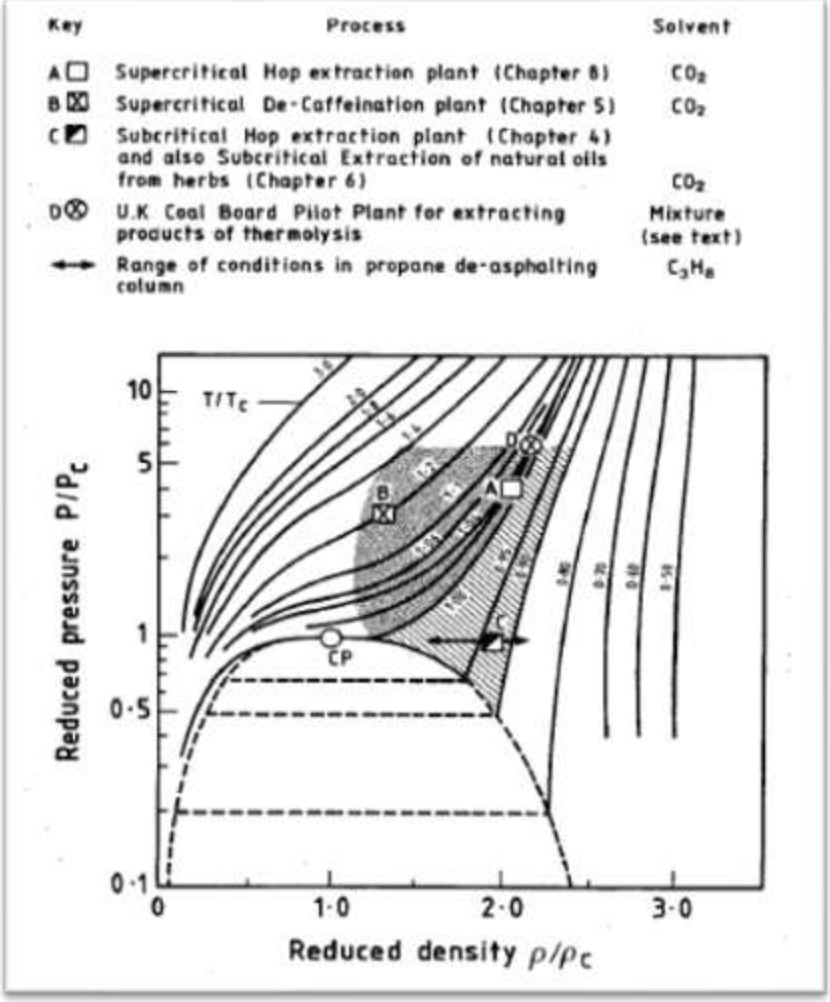


Figure 1.3.5: Range over which “near- critical” extraction operations have been reported [59]

It is important to note that working with SCF technology has different goals and challenges depend on the scope of the work. In the case of researching work in a laboratory scale with SCF, the goal is to achieve yields as high as possible. On the other hand, working with SCF in an industrial process, the challenge is to find solutions to mechanical issues that are present in a process at high pressure.

Supercritical fluid extraction, SFE, is used in a large quantity of research investigations, at small scale process and in large-scale process (vessels ≥ 2-5 m3) mainly related to the food industry, like decaffeination of coffee beans and black tea leaves, and the extraction of the bitter flavors from hops.

1.3.4.Supercritical carbon dioxide

Carbon dioxide is the most widely used compound in the SC extraction process although the solvent power of the CO_2 is not the highest compared with other compounds like ethane or propanol. There are other factors, besides those related to the solvent power of the carbon dioxide, that make the CO_2 the ideal agent for SC processes, such as factors related to the process of extraction itself and the product obtained.

The principal characteristics of scCO2 are:

- ✓ GRAS (generally regarded as safe)
- ✓ Gentle conditions (pc=73.8 bar; Tc=31.1 ºC)
- ✓ Inert, odorless, tasteless
- ✓ Easily removed from products
- ✓ Non-explosive
- ✓ Readily available, inexpensive
- ✓ Benign solvent
- ✓ Bactericide
- ✓ Completely non-reactive
- ✓ No legal constrains globally for foodstuff
- ✓ Mineral carbon dioxide is free of impurities
- ✓ No environmental effect

The factors which present more advantages for the $scCO_2$ in extraction process are:

- ✓ Selectivity: adjustable solvent power (p/T)
- ✓ Efficiency : high recovery rates, complete utilization of raw material
- ✓ Flexibility: various extraction concepts to meet target (co-solvents, fractionation)
- ✓ Image: positive natural process

The factors related with the product are:

- ✓ High quality of the products
- ✓ Retains complete raw material quality (no heat damage)
- ✓ No solvent traces (completely solvent free)
- ✓ Exceptional shelf live
- ✓ No stabilizer (or technical adjuvant) necessary
- ✓ Clean label

The carbon dioxide is obtained in large quantities as a by-product of fermentation, combustion, and ammonia synthesis and would be released into the atmosphere sooner rather or later, if it were not used as a supercritical fluid. [57]

Environmentally benign supercritical carbon dioxide is demonstrating significant potential for the development of a wide range of alternative processes that totally or partially eliminate the use of some of the most commonly used organic solvents. The rapid mass transfer properties associated with the lower viscosity of SCF carbon dioxide can bring about more time efficient production capabilities for various types of important industrial processes.[61]

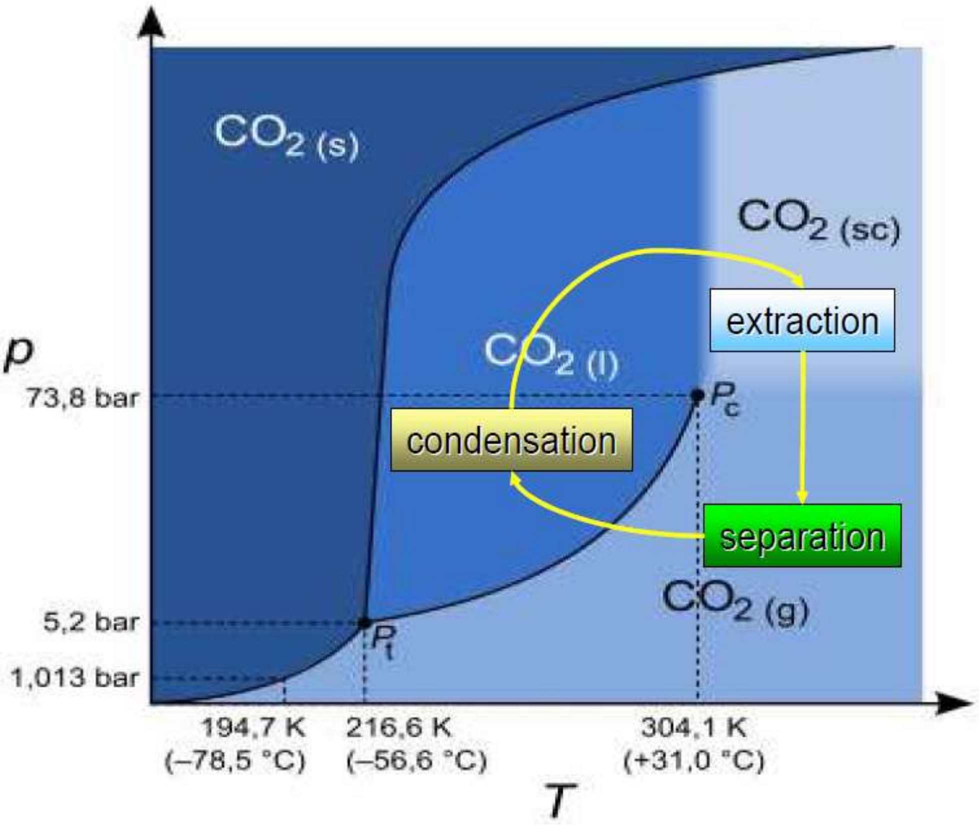


Figure 1.3.6: CO_2 phase diagram

The solvent power depends on density and vapor pressure of the solute. The density can be adjusted by the temperature and pressure parameters, and in the other hand the vapor pressure can be adjusted by changing the conditions on the temperature. This means that using the same raw material as a starting point and using CO_2 as extract agent, at different conditions could separate different compounds, only adjusting and combining these two parameters, temperature and pressure in order to obtain the desire compound.

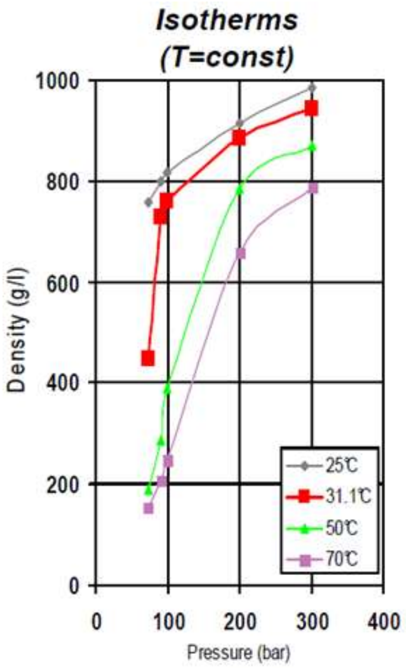


Figure 1.3.7: Solvent power of sc-CO_2.Density as function of pressure [59]

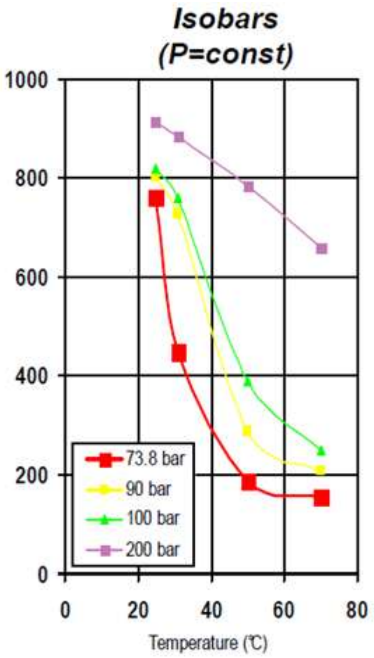


Figure 1.3.8: Solvent power of sc-CO_2.Density as function of temperature [59]

Actually it must be taken into account that the scCO2 is a poor solvent for most substances in comparison to common organic solvents. Its polarity character as a solvent is intermediate between a truly nonpolar solvent, such as hexane, and weakly polar solvents. But its capacity as solvent and its selectivity can be improve by adding co-solvents. The most usually co-solvents added to the $scCO_2$ are water, ethanol, methanol, and mixtures of water-ethanol. They are be added in proportions about 5-10%.

Authors Brunner and Del Valle & Aguilera [56] were summarized in their works a few rules for the solvent power of $scCO_2$:

- ✓ It dissolves non-polar or slightly polar compounds
- ✓ The solvent power for low molecular weight compounds is high and decreases with increasing molecular weight
- ✓ SC-CO2 has high affinity with oxygenated organic compounds of medium molecular weight
- ✓ Free fatty acid and their glycerides exhibit low solubility
- ✓ Pigments are even less soluble
- ✓ Water has a low solubility (<0.5% w/w) at temperatures below 100 ºC
- ✓ Proteins, polysaccharides, sugars and mineral salts are insoluble

- ✓ Its capability of separating compounds that are less volatile, have a higher molecular weight and/or are more polar, as pressure increases.

1.4. CATALYST FREE DIRECT TRANSESTERIFICATION IN SUPERCRITICAL METHANOL

1.4.1. Catalyst free supercritical method vs. catalytic method

As was mentioned in the methods of production of biodiesel, chapter 1.2.2, bases and acids are used as catalyst in conventional tranesterification of vegetable oils, but at the same time, these methods, including enzymatic catalytic method, have proven to be very sensitive to the presence of water and free fatty acids. Catalyst-free reactions with alcohols at high pressure and temperature provide improved phase solubility, decrease mass-transfer limitations, afford higher reaction rates and make easier separations and purifications steps of product [62].

	Catalytic MeOH process	**SCM method**
Methylating agent	Methanol	Methanol
Catalyst	Alkali (NaOH or KOH)	None
Reaction temperature (K)	303-338	523-573
Reaction pressure (MPa)	0.1	10-25
Reaction time (min)	60-360	7-15
Methyl ester yield	96	98
Removal for purification	Methanol, catalyst, glycerol, soaps	Methanol
Free fatty acids	Saponified products	Methyl esters, water
Smelling exhaust	Soap smell	Sweet smelling

Figure 1.4.1: Comparison between catalytic methanol method and supercritical methanol method for biodiesel form vegetable oils by tranesterification [46]

In supercritical conditions, the mixture between methanol and triglycerides becomes a single homogeneous phase, which accelerates the reaction because there is no interphase mass transfer to limit the reaction rate. In addition, the non-catalytic supercritical process has environmental advantages because there is no waste generated as a result of catalyst treatment and separation from the final product. Furthermore, this non-catalytic method requires no pretreatment of the feedstock because impurities in the feed do not strongly affect the reaction. When water and FFAs are present in the feed, three types of reaction (transesterification, triglyceride hydrolysis and alkyl esterification of fatty acids) occur simultaneously. Alkyl esterification is faster than transesterification and ensures that all FFAs in the feed whether present originally or as products of hydrolysis, are completely transformed into fatty acid alkyl esters [63].

1.4.2. Continuous process vs. batch process

A continuous catalytic tranesterification of vegetable oils to FAME, has been proposed as early as 1940s, and studied until recently. For larger capacity commercial production, a continuous transesterification process is preferred over batch process due to the requirement of consistent product quality and low capital and operation cost per unit of product [64]. In continuous mode, direct transesterification with supercritical method appears as an attractive application, assuring a competitive cost to biodiesel fuel.

1.4.3. Oil extraction and transesterification reaction in one single step process with supercritical methanol and supercritical methanol/CO_2 mixtures

A different approach to the biodiesel production process can be applied by taking advantage of the characteristics of supercritical fluids, namely their ability to be used as extraction agents and reaction solvents. More specifically, in the case of supercritical methanol it can also act as reactant, as seen in the previous chapter. In this case supercritical methanol could act as triglyceride extraction agent and simultaneous direct transesterification reaction solvent and reactant. It is therefore possible to integrate two distinct process into one single step.

It is the case of system studied in this work, there are two processes occurring at the same time in a packed bed reactor full of SCG: the extraction of the oil of the SCG, and the trasesterification reaction of that oil into FAME. Each one of these processes are affected and depend of some parameters, which were studied in order to optimize the efficiency of the total process.

In the case of the supercritical extraction of oil, the flow pattern of the solvent (methanol) into the packed bed, the mass transfer resistance and the solubility of the triglycerides in the solvent, are the main parameters that affect more directly the efficiency of the process. As it had been explained in the chapter 1.3.2., the solvent power of a supercritical fluid (solubility of a component in a supercritical fluid) is the most important aspect of a solvent/solute system to be used in a SCE. Is necessary when selecting the solvent, to know the appropriate conditions of state, comprising all existing phases at equilibrium and their behavior with respect temperature and pressure [58].

In the case of the transesterification reaction process, the aspects to consider for the efficiency of the process are the kinetics of the reaction and the mass transfer resistance. Even though the kinetic model for this particular systems of simultaneous extraction-reaction, is not well known, is important to determinate the optimal reaction conditions, mainly volume flow of methanol, temperature and pressure, to achieve the best values for FAME yield. There are limited data from the effect of the pressure in on FAME production with supercritical methanol because the reactions have principally been conducted in batch reactors, where the pressure cannot be controlled independently from the density. It had been reported that the effect of the increase pressure in the tranesterification reaction at supercritical conditions has a positive effect in the yield of FAME below 20MPa witih the temperature range of 547- 623 K. But this effect decrease avobe this pressure. The temperature had been reported to be the most critical parameter for determining the extend of the reaction, especially across the critical temperature of the methanol (513 K), the FAME content level rises 2-3 fold as themperature increases from 473- 623 K at constant pressure and methanol to oil molar ratio. Influence of the temperature has a strong influence on the reaction rate, On the other hand, excessively high temperature can lead negative effect on the FAME content. This effect can be produced by thermal degradation reactions. Thus it had been indicated an appropiete temperature for biodiesel production with supercritical methanol lower than 673 K, and is is preferably work under 543 K where the maximum FAME content in biodiesel can be obtained [65]

CO_2 is used as a co-solvent in the process in order to allow working in milder conditions of temperature, which allows reducing amounts of energy employed and the cost of operation in the case of the process will be scaled-up. Supercritical conditions of methanol and CO_2 are 513 K, 8.0 MPa and 304 K, 7.38 MPa respectively. Is important to operate in lower values of temperature, as Imhara et al. has suggested, in some cases, the high temperatures and pressure needed in transesterification with SCMeOH could cause degradation of the fatty acid esters formed. In the conditions of 673 K and 15 MPa, Sawangkeaw et al. proposed possible side reactions between SCMeOH or SCE and palm oil as: hydrolysis of triglycerides, thermal cracking of unsaturated fatty acids, etherification of glycerol, isomerization of oleic acid and methyl oleate and decarboxylation of fatty acid.

CHAPTER 2: MATERIALS AND METHODS

2.1. MATERIALS

2.1.1. Chemicals

The SCG used in all tests was provided by Delta Cafés ®

All the compounds used in this experimental work and all their associated information are represented in the next table.

Table 2.1.1: Compounds used in the experimental work description

Name	Molecular Formula	Molecular Mass (g/mol)	% Purity	Brand
Methanol	CH_4O	32,04		
Carbon Dioxide	CO_2	44,01	$\geq$99,98	Air Liquid
Hexane for Chromatography	C_6H_{14}	86,18	97	Sigma-Aldrich

2.1.2. Equipment

The equipment used during the experimental work was the following:

- Analytical balance METTLER TOLEDO, model PJ12;
- Temperature and Process Controller HORST, model HTMC1;
- PT100 sensor;
- Internal thermocouple type K;
- Back Pressure Regulator (BPR) TESCOM, model 27-1700;
- Cryostat HAAKE, model EK12;
- Recirculation pump Julabo, model FT400;
- Flow controller Rheonik, model RH 007;
- Liquid pump Minipump®, model LDC Analitical;
- Air Driven Liquid Pump Schmidt, Kranz and Co, model Maximator M11 CO_2;

2.1.3. Experimental set-up

The continuous biodiesel production process apparatus is shown in the next figures. For the experiments of tranesterification only with ScMeOH, correspond the figure 2.1.1, and for the experiments of transesterification with ScMeOH and CO_2 mixtures correspond the figure 2.1.2.The difference between the two configurations is the line of CO2 in the figure 2.1.2.

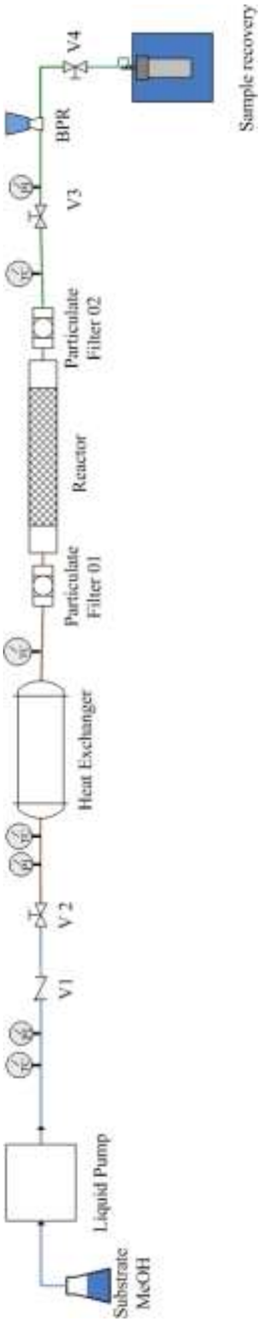
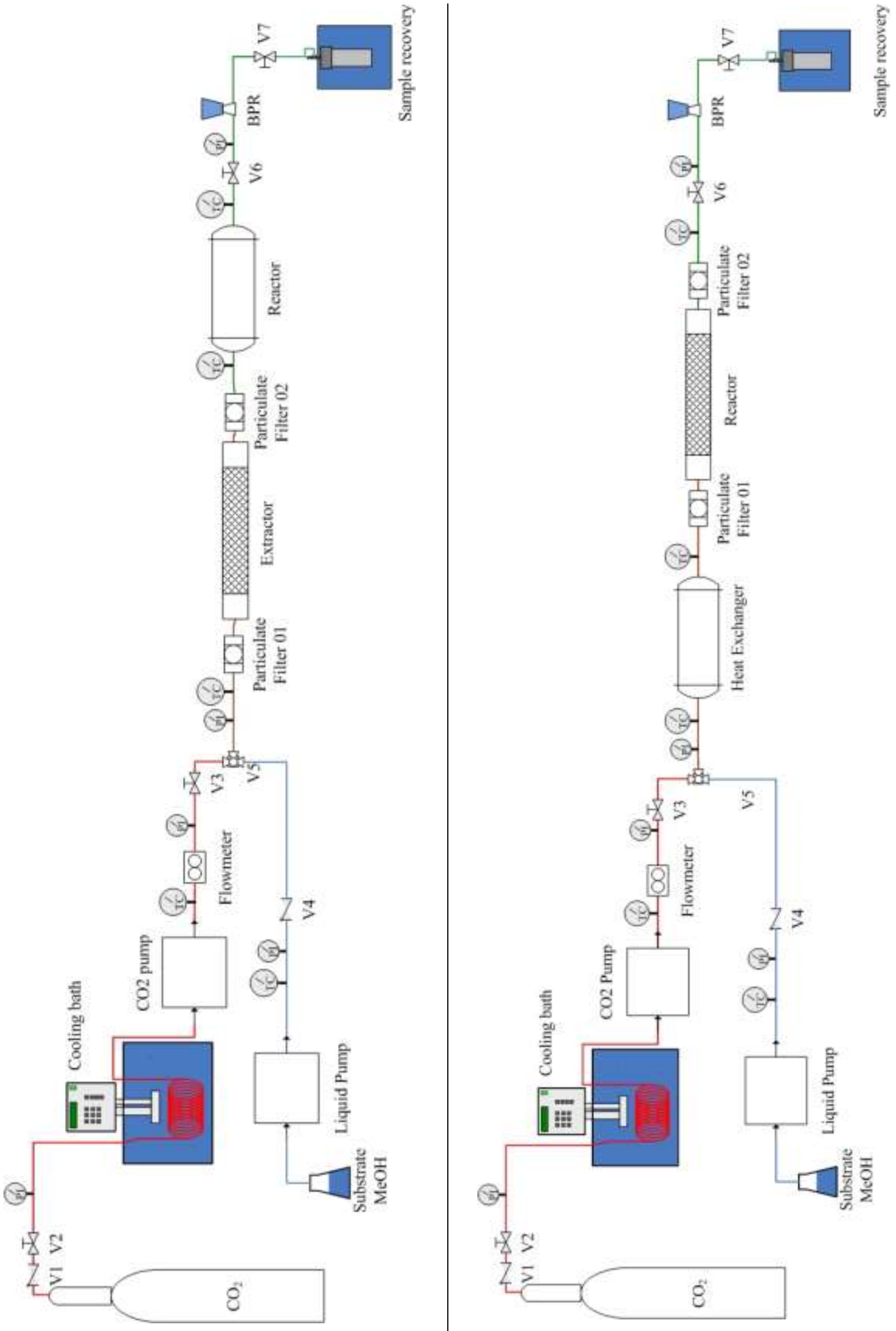


Figure 2.1: Experimental Set-up (I)



Model A

Model B

Figure 2.1.2: Experimental set-up (II)

2.1.4. Continuous Biodiesel production Apparatus

The main sections of this apparatus are the heat exchange section and the reaction section. The samples are recovered after the BPR valve, wich control the pressure of the system, at the end of the installation. In the next figures are represented the principal sectors of the installation:

Figure 2.1.3: Overview of the apparatus used in this work

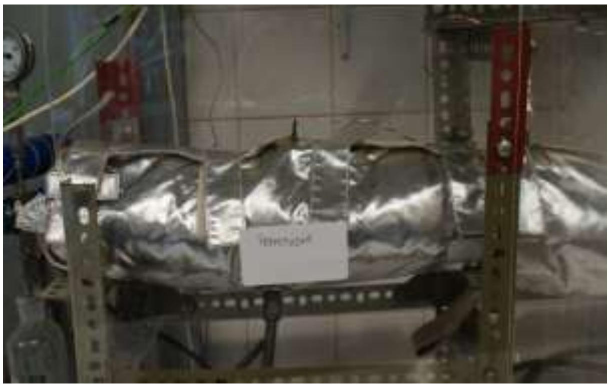


Figure 2.1.4: Heat exchanger section

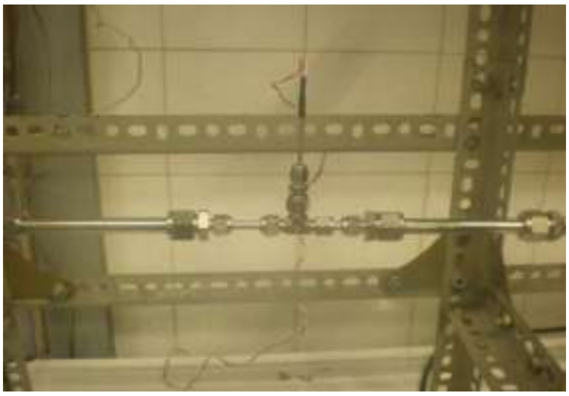


Figure 2.1.5: Stainless steel heat exchanger

Figure 2.1.6: Reaction section

Figure 2.1.7: Stainless steel reactor

Figure 2.1.8: Separation section. BPR Valve

This apparatus is composed by a CO_2 vessel followed by a water/ ethylene glycol refrigeration system (Julabo®, model FT400), to liquefy the carbon dioxide and allow it to be pumped by a CO_2 pump, (Air Driven Liquid Pump Schmidt, Kranz and Co®, model Maximator M11 CO2), the flow rate of CO_2 in this line is measured by a flow meter (Rheonik®, RH 007). There is other line with a Methanol vessel followed by a liquid pump (Minipump®, model LDC Analitical, max. flow 10 ml/min). The two lines come together in third line after a mixing valve. The mixture is pumped to the heating section before passing through the packed-bed reactor, already field with SCG.

The heat exchanger consists in a tubular stainless steel vessel, with an inner diameter of 10,5 mm and total length of 140.20 mm, filling of small spherical stainless steel balls, which allow improving the heating inside the exchanger, and with a PT100 sensor, in order to measure and control the temperature. The reactor is consisted in a tubular stainless steel vessel, 10,5 mm of the inner diameter and 127.62 mm of length, there is a PT100 sensor inside the reactor, in order to measure and control the temperature. Before and after the entire set of tubes forming the packed bed reactor full with the SCG, there are two brass in-line particulate filters (Swagelok®, 1/8 in., Female NTP, 0.5 micro pore sizes). The heat exchanger and the reactor are heated and controlled by two temperature and process controllers (HORST, model HTMC1) which are pre-programed with a progressive sequence of temperatures until reach the temperature of the experiment. The reaction pressure is controlled with a steel stainless back pressure regulator valve (BPR) (Tescom Europe®, 26-1000) with a maximum input pressure of 690 bar, and it is measured by an analogical pressure meter (WIKA, 640.059) with an interval of 20 bar. To avoid freezing caused by the decompression of the CO_2, the BPR is heated up with an electrical heater.

The products-CO_2 mixture obtained after the reactor, which until now has always been in one phase region, are decompressed afetr the back pressure regulator valve (BPR), and the sample are collected after the exit of the BPR in a vial. The CO_2 is evaporated when in contact with the atmosphere, and the Methanol phase is collected in a vial immersed en un ice bath, to prevent the possible evaporation.

All the high pressure tubing, valves and fittings are from HIP®, SWAGELOK® and Tescom Europe®

2.2. METHODS

2.2.1. Continuous Biodiesel production

- Direct transesterification of spent coffee grounds oil in supercritical methanol

At first an amount between 1.5-2.5 g of SCG was weighed an putting inside the reactor fixed bed, then the system was closed and the leaks were checked, pumping methanol trough the pipes and adjusting the pressure of work with the regulation of the BPR valve. After that, the pump of methanol was stopped and the heating system was turn on. The heater controllers were programmed with a sequence of temperatures until reach the desire value, in order to achieve slow and easy replicate way of heat the system in each experiment. The pressure and the temperature were different from one experiment to another, but they always were above the P_c and the T_c of the methanol, 8MPa and 513 K respectively. When the thermocouple of the heat exchanger and the reactor show the same temperature inside the tubes, the HPLC pump of methanol was turn on. The samples were collected,every 10 minutes, at the end of the BPR valve in vials at room pressure and immersed in an ice bath since the first drop of product fall into the vial. The samples were recovered along 60 minutes for further analysis.

- Direct transterification of spent coffee grounds oil in supercritical methanol/CO2 Mixtures

At first an amount between 3-4 g of SCG was weighed and putting inside the reactor fixed bed, then the system was closed. Then the refrigeration system of CO_2 was turn on when the temperature of the bath was below 273 K, and then the valve V2 was opened in order to full only the line of CO_2, so the valve V3 had to remain closed. The BPV was previously regulated with the pressure of work, 10 MPa. Slowly, the valve V3 was opened and the all system were full of CO_2. This procedure served also to check the possible leaks in the system. The pumping of CO_2 was kept constant in order to regulate the flow rate. The heat exchangers turned on, the set point for the reactor was regulated at 313 K and the set point for the reactor was regulated at 473 K. When the temperatures were achieved, the pumping of methanol started, at the flow rate selected for each experiment. The samples were collected,every 10 minutes, at the end of the BPR valve in vials at room pressure and immersed in an ice bath since the first drop of product fall into the vial. The samples were recovered along 60 minutes for further analysis.

2.2.2. Sample Analysis

- **Evaporation of methanol of the sample**

Figure 2.2.1: Samples collected with methanol

After the experimental run, the collected samples were weighed in an analytical balance (METTLER TOLEDO, model PJ12).

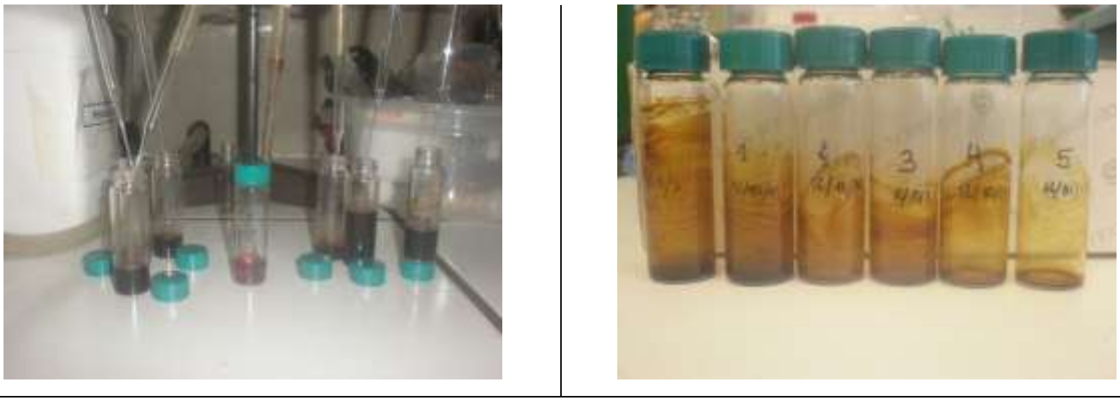


Figure 2.2.2: Samples collected dry of methanol

The evaporation of methanol from the samples is performed by bubbling air into the collected samples. The air stream first passes through a molecular sieves packed bed in order to remove the moisture from the air and then by a flow regulator (Parker Pneumatic, model P3D) that regulates the flow of air that goes directly into the sample.

- **Preparation with hexane and filtration**

After complete evaporation of methanol, the final sample is weighed. Next, the sample was dissolved in 5ml of a solution of hexane. However, the sample was not completely dissolved in hexane because it has a polar and a non-polar fraction.

The non-polar fraction was transferred to another vial, after a filtration, followed by evaporation of residual hexane. After the evaporation of the hexane, the dry vials were weighted and added the internal standards, IS1 and IS2, respectively, and the derivative agent MSTFA, in order to prepare the sample to be analyzed in the chromatograph, GC-MS, by the EN 14105 method.

The polar fraction was weighted in an analytical balance and registered the quantity of residue in each sample in order to know the fraction of non-oil compounds that were extracted. (METTLER TOLEDO, model PJ12)

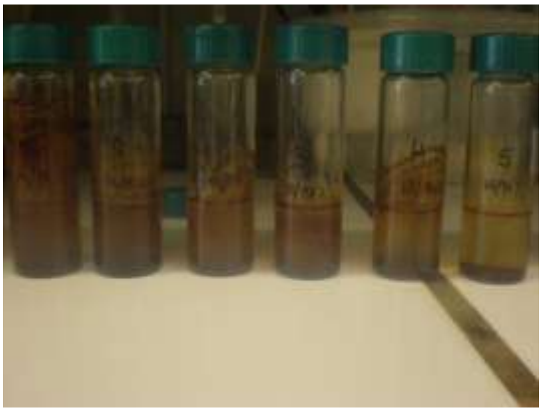


Figure 2.2.3: Samples with hexane

Figure 2.2.4: Filtration of the samples

- **Gas chromatography**

The fatty acid methyl esters (FAME), triglycerides. diglycerides, monoglycerides were determined by gas chromatography (GC) with on-Colum injection.

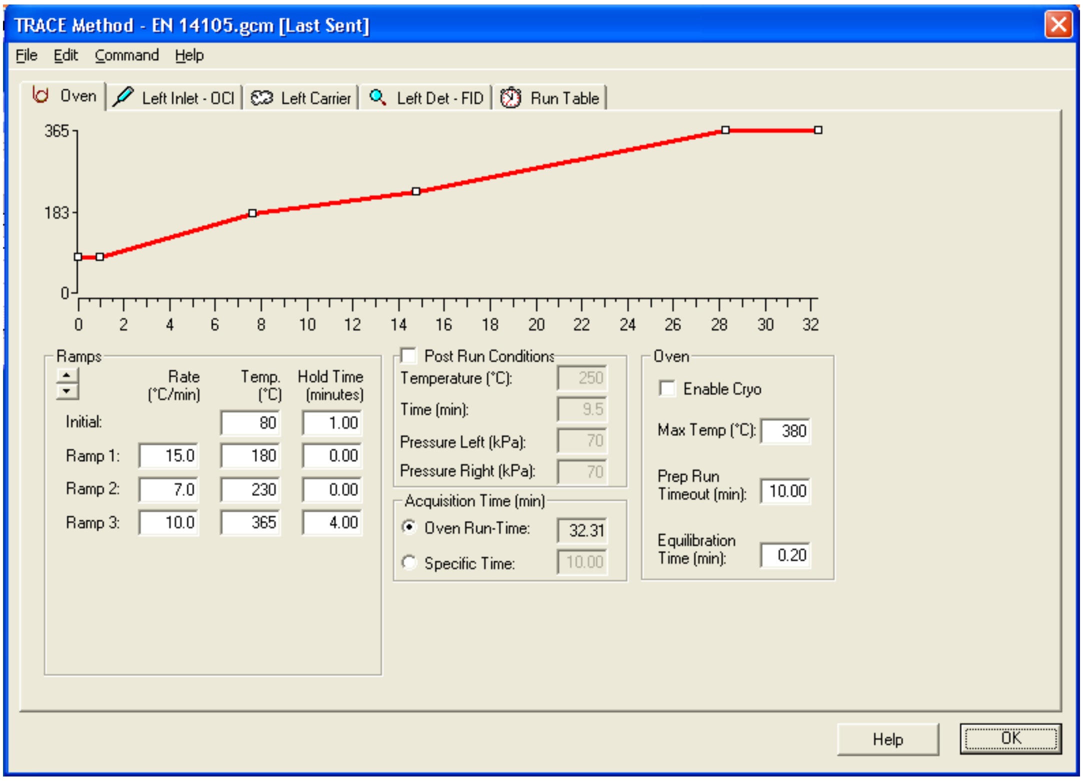
Gas chromatography technique is based on the passage of the compounds through a capillary column by the flow of inert gas which consists in the mobile phase. This inert gas can be He, Ar, N_2, ect. The column contains a stationary liquid phase absorbed to the surface in an inert solid where the sample components are retained. The compounds can be separated according to their affinity (polarity) for the stationary phase or its boiling point. An on-Column injection means that the sample injection is made directly in the injector of the column. This kind of injector allows the placement of the syringe inside the column without depressurize it.

Figure 2.2.5: Gas Chromatograph on-column THERMO SCIENTIFIC TRACE GC ULTRA

The chromatograph was a THERMO SCIENTIFIC TRACE GC ULTRA Series with a flame ionizator detector (FID) with a ZB-5HT INFERNO column, 10 x 0.32 mm, 0.10 µm film thickness and a polarity of 8 from ZEBROM. The stationary phase of the column in non-polar consisted by 55-Phenyl 95%-Dimethylpolysiloxane. Thus, the FAME, tiglycerides, diglycerides, monoglycerides are separated according to the boiling points and the unsaturated compounds are eluted before the corresponding saturated acids of the same chain length. This column allows the simultaneous analysis of tiglycerides, diglycerides, monoglycerides and FAME content.

The method used was EN 14105. The carrier gas was He with a starting flow of 0.1 ml/min during 1 minute and rises with the rate of 1.5 ml/min to 1.1 ml/min standing at this flow until the end of the program. The oven temperature was 323-453 K at 288 K/ min followed by a ramp of 280 K/min until 503 K and 303 K/min until 653 K with a final holding time 10 min. Peak identification was carried our using known standards and the software Chorm-Card

The samples preparation method is describes in Appendix C.



Ramps

	Rate (°C/min)	Temp. (°C)	Hold Time (minutes)
Initial:		80	1.00
Ramp 1:	15.0	180	0.00
Ramp 2:	7.0	230	0.00
Ramp 3:	10.0	365	4.00

☐ Post Run Conditions
Temperature (°C): 250
Time (min): 9.5
Pressure Left (kPa): 70
Pressure Right (kPa): 70

Acquisition Time (min)
● Oven Run-Time: 32.31
○ Specific Time: 10.00

Oven
☐ Enable Cryo
Max Temp (°C): 380
Prep Run Timeout (min): 10.00
Equilibration Time (min): 0.20

Figure 2.2.6: Method EN 14105 description

- ❖ Sample analysis

Trough Chrom-Card Software, an analyzed of the chromatogram is made. An example of a typical chromatogram is described in the figure 2.2.7:

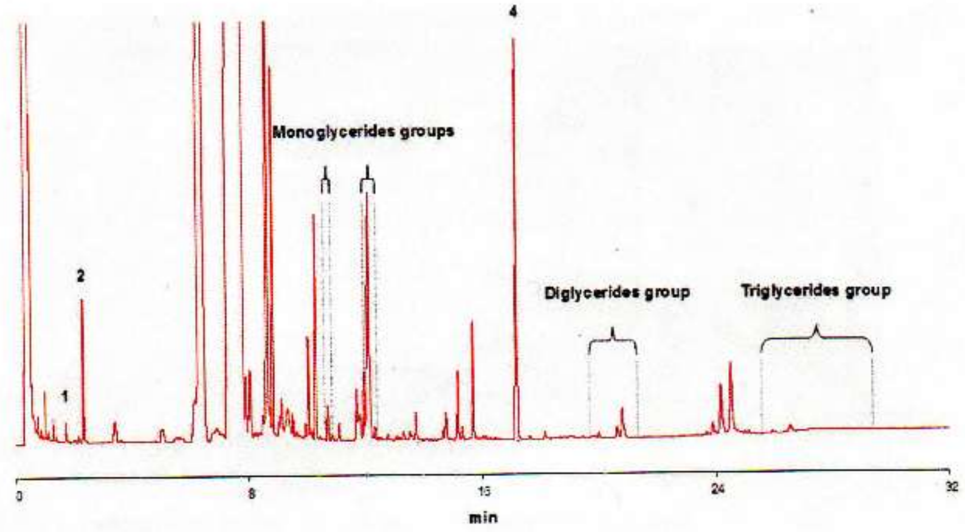


Figure 2.2.7: Typical chromatogram obtained by GC

The first peak (1) corresponds to the glycerin. The second peak (2) corresponds to the internal standard 1 (IS1) and the third peak corresponds to the internal standard 2 (IS2).

CHAPTER 3: RESULTS AND DISCUSSION

3.1. DIRECT TRANSESTERIFICATION IN SUPERCRITICAL METHANOL

For these series of experiments, the configuration of the installation used was described in the figure 2.1.1., setup (I), in the chapter 2.1.3. The extraction and the reaction took place in the packed bed reactor at the same time. Operating at different conditions of methanol flow, pressure and temperature it was determined the optimal conditions for the maximum yield of the global process, the optimal conditions for the maximum yield of oil extracted and the optimal conditions for the maximum yield of FAME obtained.

The yield of oil extracted indicates the quantity of TG extracted in the process from the initial oil in the SCG. It was messured from the amount of oil extracted and not reacted, the FAME generated, the DG, MG that are present as impurities. The initial oil in the SCG was about 10% of the initial mass of SCG in the reactor. It was reference at the efficiency of the oil extraction in the process.

$$Yield\ \ oil\, extracted\ (\%) = \frac{mol\ total\ oil\ extracted}{mol\ oil\ in\ SGC} \times 100$$

Equation 3.1: Calculation yield of oil extracted (%)

The yield of FAME indicates the moles of oil extracted, that were generated into FAME in the transesterificated reaction with ScMeOH. Transesterification of vegetable oil into FAME is a three step series of reversible reactions; the conversion of triglycerides is not equal to the FAMEs content in each sample, due to the formation of intermediate species. If the reaction is not completed, there will be diglycerides and monoglycerides, present in the final product.

$$FAME\ Yield\ (\%) = \frac{mol\ FAME\ generated}{3 * mol\ total\ oil\ extracted} \times 100$$

Equation 3.2: Calculation FAME yield (%)

The yield of the process is referred to the efficiency of the global process. Is the result of the efficiency of the extraction plus the efficiency of the reaction of the oil into FAME. There are some possible scenarios:

- ➢ High extraction yield and low reaction yield. In this case it is obtained a high amount of final product, biodiesel, with a high content of impurities, DG ans MG.

- High extraction yield and high reaction yield. In this case it is obtained a high amount of product with a high puriry.
- Low extraction yield and low reaction yield. In this case it is obtained a low quantity of final product with a high content of impurities.
- Low extraction yield and high reaction yield. In this case it is obtained a low amount of final product with a high purity.

The analysis of the results would indicate in each case which is the limitation step in the process; either the diffusion or the kinetics of the reaction. In this case of tranesterification reaction under supercritical conditions the effect of the diffusion is not very significant because the methanol is employed as solvent and as reagent agent, thus the particles of solute are totally sorounded by methanol and there are not diffusional problems of the solute in the medium.

$$Yield\ of\ the\, process(\%) = \frac{mol\ FAME\ generated}{3 * mol\ oil\ in\ SGC} \times 100$$

Equation 3.3: Calculation of yield of the process (%)

3.1.1 Influence of the flow rate of methanol in the yield of oil extracted (%), FAME yield (%), and total yield of the process (%)

According with the transesterification reaction stoichiometry, 1 mole of oil reacts with 3 mole of methanol. However, in order to achieve a high yield in the total process the molar ratio oil: methanol must be higher than 1:3. By increasing the oil to methanol molar ratio the reaction equilibrium is shifted in the direction of product formation. In the case of this work the process was stablished in semicontinuous mode where the methanol was always pumped in excess respect to the oil,. The methanol is in these case the solvent and the reagent of the process, thus was more appropriated to study the effect of the flow rate of the methanol (ml/min) instead of the effect of the methanol: oil molar ratio.

The transesterification reaction was studied for the following volume flow rates of methanol: 1ml/min , 3ml/min; 5 ml/min, and the conditions of the process were P= 10 MPa and T= 573.15 K

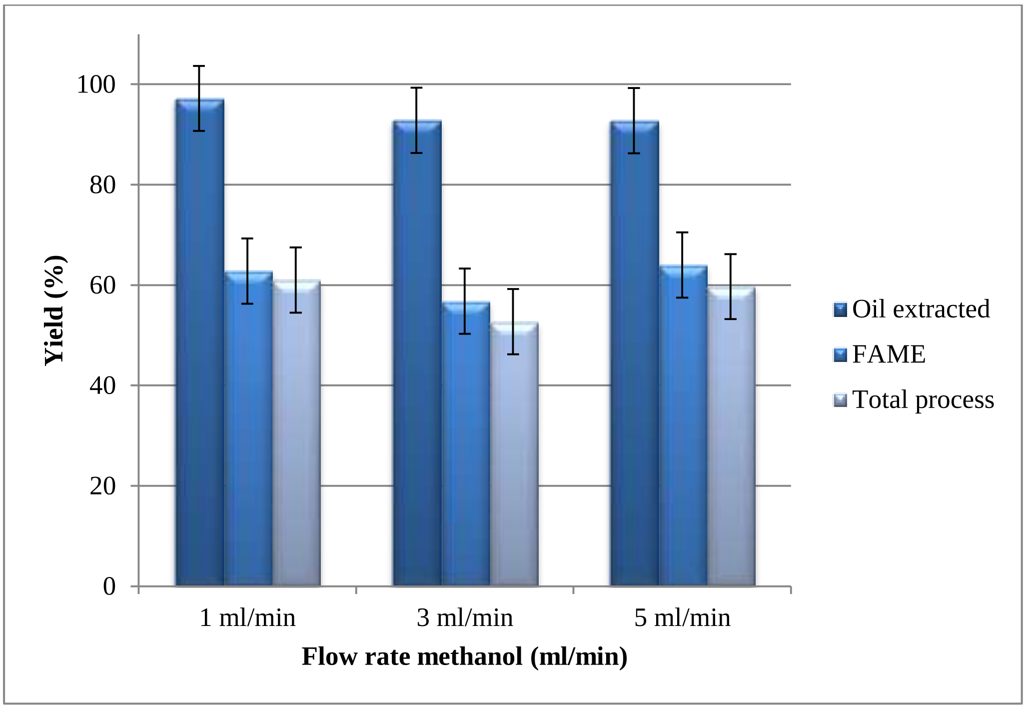


Figure 3.1.1: Influence flow rate of methanol (ml/min) in the yield of oil extracted (%), FAME yield (%) and total process yield (%), at 10MPa and 573.15 K

The optimal conditions for the maximum yield in the process, 61%, correspond to 1 ml/min of methanol at P=10 MPa and T= 573.15 K. In this case the extraction of oil is almost total, 97% The results for the two other flow rates experimented follow the same tendency, with results above 90% in the yield of oil extracted. However the efficiency of the reaction into FAME presented values above 60% yield for both 1ml/min, 3 ml/minand 5 ml/min.(see figure 3.1.1). The effect of the lower value for the FAME yield coul be caused by posibles side reactions in this experiment as hydrolysis of triglycerides, thermal cracking of unsaturated fatty acids, isomerization of oleic acid and methyl oleate. The formation of other components instead of FAME due to thermaldegradation reactions was reflected n the low yield of FAME obtained.

3.1.2 Influence of the pressure in the yield of oil extracted (%), FAME yield (%) and total yield of the process

The influence of the pressure in the efficiency of the process as well as the yield of oil extracted and in the FAME yield was tested at the conditions of T=533.15 K, 1 ml/min of methanol and three values for the pressure: 10 MPa, 15 MPa and 20 MPa. The results are shown in the next figure:

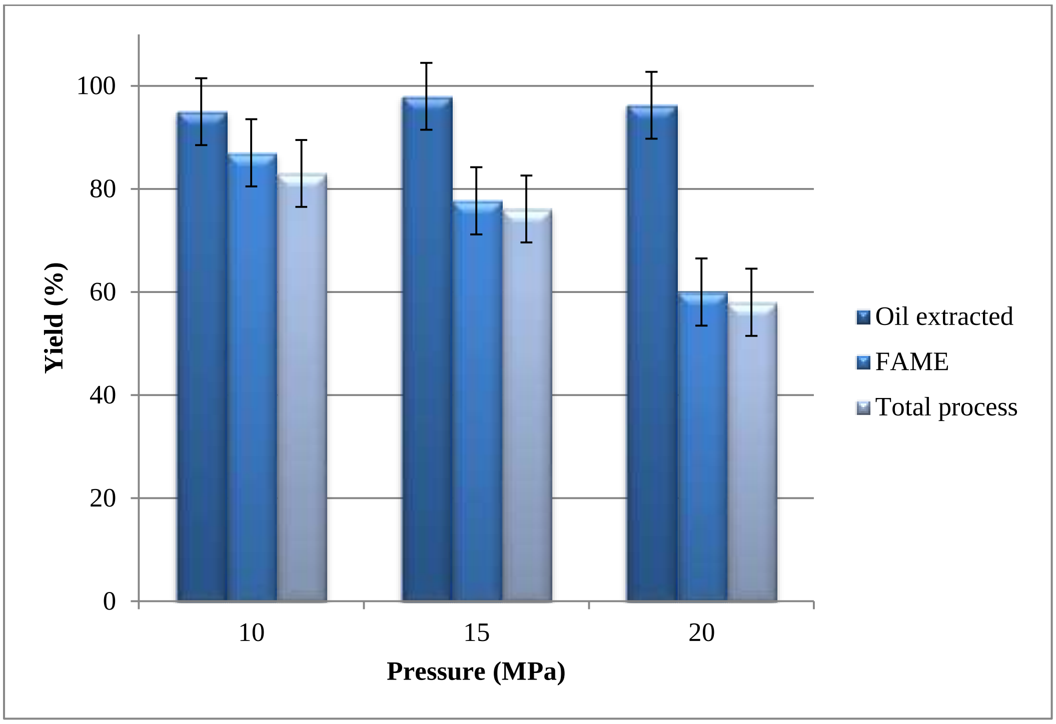


Figure 3.1.2: Influence of the pressure in in the yield of oil extracted (%), FAME yield (%) and total process yield (%), at 533.15 K and 1ml/min of methanol

The optimal conditions obtained for these experiments are P= 10MPa, T= 533.15 k and 1ml/min of methanol. The maximum yield of the process obtained was 83%. At these conditions the yield of oil extracted was 95% and the yield of the reaction was 87% (Figure 3.1.2). The pressure does not manifest any effect in the extraction of oil from the SCG. However the yields of the reaction of FAME experiment a reduction when the pressure was increased.

It is suggested that the conversion of FAME increase with the pressure at constant temperature. Below 20MPa, the reaction pressure affects the FAME content significantly within the temperature range of 543- 623 K, but the effect decrease below this temperature [65].

It was observed in experimental works that with the increase of the pressure it was obtained a “crude like” product, more dark and with high viscosity. This product was not possible to analyzed its composition. Thus indicates that high pressures induced other reactions instead transesterification of the TG, that generated unknown products,in such away the amounts of FAME collected in these experiments were lower than the expected.

P= 10 MPa P= 15MPa P= 20MPa

Figure 3.1.3: Samples of experimetns at P= 10MPa, P= 15 MPa and at P= 20MPa

3.1.3 Influence of the temperature in the yield of oil extracted (%), FAME yield (%) and total yield of the process

Experiments were performed to prove the influence of the temperature in the yield of triglycerides extracted and in the yield of FAME generated. The experiments were done at 10 MPa of pressure, 1ml/min of methanol and at 533.15 K, 573.15K and 603.15 k respectively.

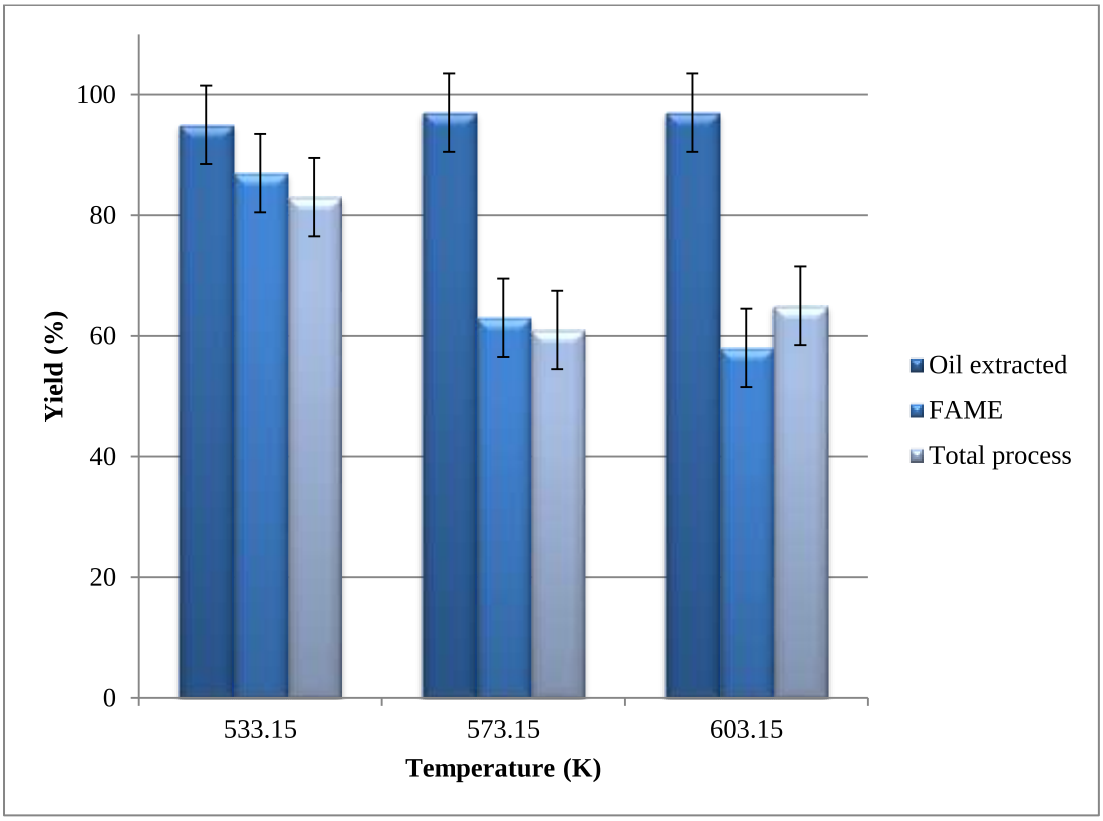


Figure 3.1.4: Influence of the temperature in the yield of oil extracted (%), FAME yield (%) and total process yield (%), at 10MPa and 1 ml/min of methanol

The maximum yield of total process obtained in these experiments was 83%, at the conditions of 533.15 K, 10MPa and 1ml/min of methanol. At those conditions the yield of the extraction of triglycerides was 95% and the yield of reaction into FAME was 87%, which means that almost all oil available in the SCG was extracted and the final product had 13% of impurities. The obtained results indicate that the yield of the reaction decrease in that case with the increasing of temperature. It has been reported that temperature has a strong influence on the conversion rate of the oil into FAME [65]. Although a high temperature enhances the rate of reaction and the amoung of FAME generated, and excessively high temperature can lead to a negative effect on the FAME content caused by thermal degradation of fatty acids. This effect was reported to happened within the temperature range of 593-623 K. Nevertheless the result obtained point out that the same degradation effect was obserfved in our case at lower temperatures (573 K). This effect of thermal degradation affect mainly unsaturated fatty acid, that is a prominent concerning in the selection of the triglyceride source, and favors against those sources with a high level of unsaturated fatty acids [65]. Imanhara et al. indicates that the appropriate temperature for biodiesel production with ScMeOH in a isothermal system is lower than 573 K, and is preferably less than 547 K, so that the maximum FAME content in the biodiesel can be obtained [66].

Figure 3.1.5: SCG after exteriment at 603.15 K, 10 MPa, 1ml/min methanol

3.2. DIRECT TRANSESTERIFICATION WITH SUPERCRITICAL METHANOL-CO_2 MIXTURES

The synthesis of biodiesel by supercritical alcohols is limited due to high equipment costs involved, as the conditions of work, temperatures and pressures are very high. Nowadays research studies focus on working at milder reaction conditions. One way to achieve this is with the use of co-solvents, like carbon dioxide. The conditions for $scCO_2$, T_c= 304 K and P_c= 7.3 Mpa, are lower than the conditions for supercritical methanol, T_c= 513 K and P_c= 8.0 Mpa . In addition, CO_2 enhances the mutual solubility of the oil-alcohol mixture, reducing the transport limitations and increasing the reaction rates [62].

It had been realized experiments with methanol and CO_2 as co-solvent in the same installation that was used for the previous experiments with pure methanol (see figure 2.1.1.). Initially, the configuration of the installation did not allow to obtain representative results. For low and high values of flow rates, 1 ml/min and 5 ml/min respectivelly, the recovery of samples presented important problems. Thus a solution was proposed in order to over come this problem. The configuration of the initial installation was changed separating the one single step process into a two consecutive steps process (see figure 2.1.2, Model A). The first step consisted in the separation of the oil, in which spent coffee grounds was placed inside a packed bed. The second step of the process was the reaction of the oil extracted in the previous step, in a reactor. This reactor consisted in a tube of stainless steel full of small balls, to enhance the mixing between the solvent and the soltute. For the total process, it was stablished P= 10MPa, (optimum pressure already studied in section 3.1.2). The temperature conditions were different for each one of the steps. Because in the first step took place the extraction of the oil and the solvent used was the mixture of methanol with CO_2, the value for the temperature of operation was stablished at 314 K, avobe the critical temperatue of the CO_2. In the case of the reaction step, it was convenient that temperature was above the critical temperature of the mixtures, a little bit below that the critical temperature of methanol, it was stablhised at 473 K. Using these alternatives was ensured to carry out the experiments with the methanol-CO_2 mixtures in supercritical conditions, at differents flow rates.

The effect of methanol-CO_2 mixtures flow rates on the yield of extracted (%), yield of FAME (%) and total yield of the process (%), at 10 MPa, 314 K for the extraction step and 473 K for the reaction step,was investigated.

3.2.1. Influence of addition of co-solvent CO_2 in the yield of oil extracted (%), FAME yield (%) and total yield of the process

Experiments were performed at different volume flow rates of solvent, with different fractions of CO_2 in methanol as represented in the next table:

Table 3.2.1: volume fractions of CO_2 experimented

Volume flow methanol-CO_2 (ml/min)	**Volume fraction CO_2 (v/v)**	Mass fraction CO_2 (m/m)
3.00	0%	0%
3.13	4%	5%
3.46	13%	16%
4.13	27%	30%
7.83	62%	66%
14.91	80%	83%

The effect of the flow rate and volume fraction of CO_2 in the yield of oil extracted is presented in the figure 3.2.1.The maximum yield obtained was 97% when the flow rate was 4.13 ml/min with and volume fraction of the CO_2 of 27%. Above this value, the amount of triglycerides extracted were smaller, thus the flow rate of solvent was increased and the residence time inside the extraction section was not enough to saturate the solvent with solute, therefore the steady state at 62% and 80% fraction of CO_2 was not achieve.

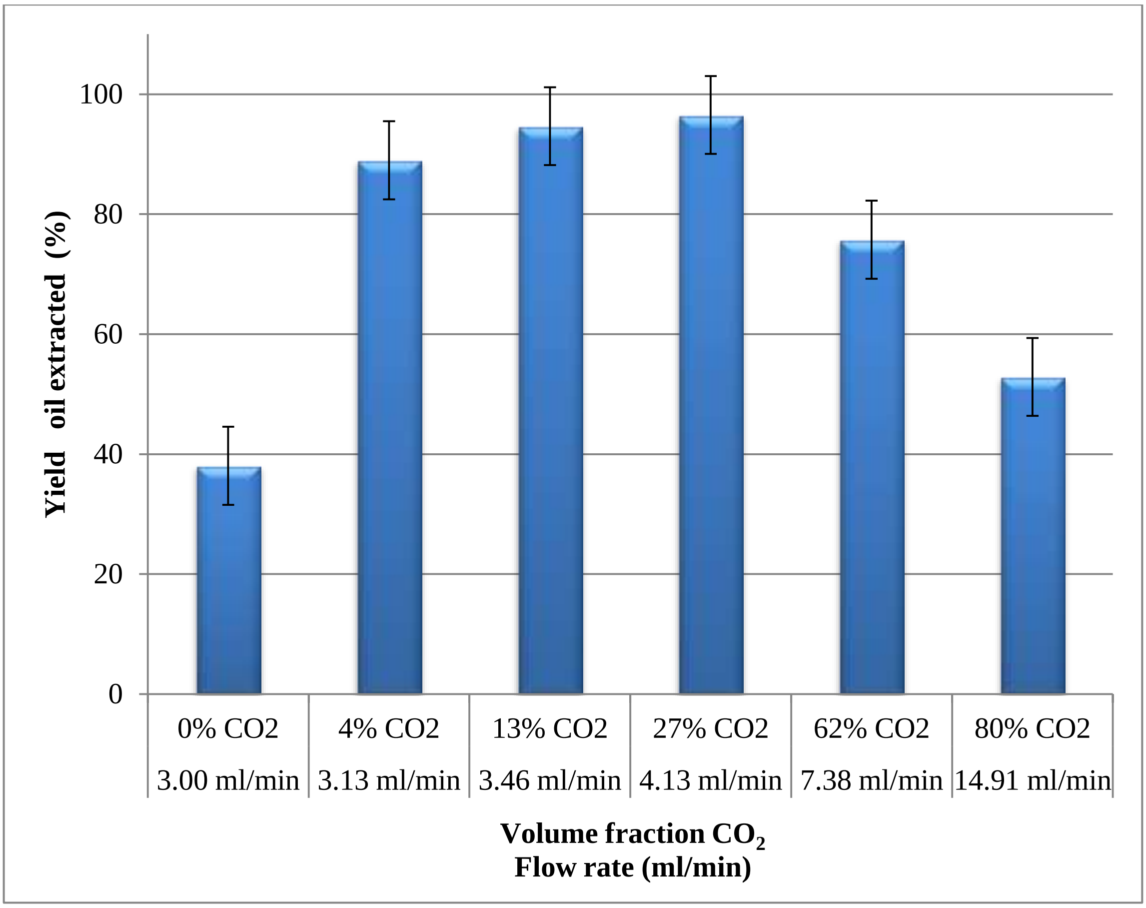


Figure 3.2.1: Influence of the flow rate and volume fraction of CO_2 in the yield of oil extracted (%)

The effect of the flow ratio and CO_2 fraction (v/v) in the FAME yield (%) is shown in the next figure (3.2.2). It haD been is demonstrated that the increase of the flow ratio did not show a substantial influence in the FAME generated, since the solvent and co-solvent were present in a large excess for each experiment. However at high flow rates, (7.38 ml/min and 14,91 ml/min), it was observed a little decrease in the yield of FAME, possibly caused because the high velocities of the solvent.

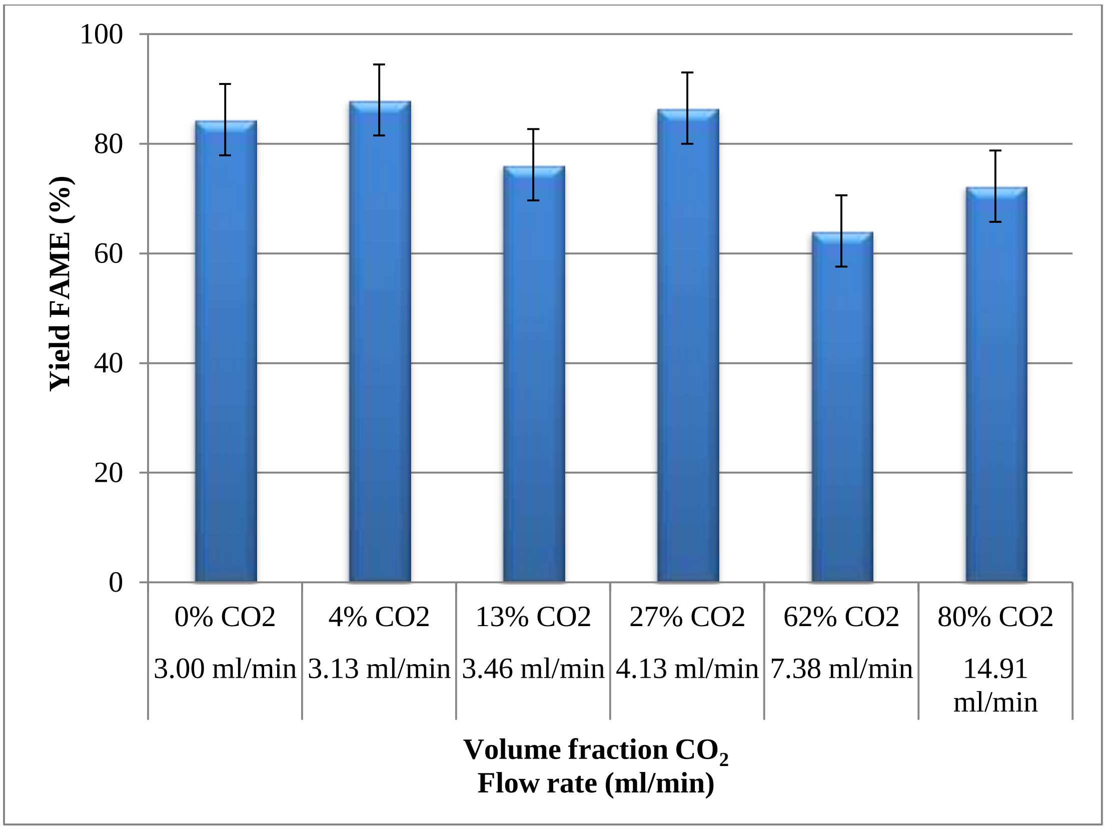


Figure 3.2.2: Influence of the flow rate and volume fraction of CO_2 in the FAME yield (%)

The effect of the flow rate and CO_2 in the total process yield (see figure 3.2.3) had been demonstrated that the use of CO_2 as co-solvent in the transesterification reaction with methanol under supercritical consitions has a positive effect, under a range of CO_2 of 4% - 27 % (v/v)..

Comparing the best result obtained in these experiments (methanol-CO_2 mixtures), with the results of the experiments using pure methanol (see figure 3.1.1), the yields for oil extracted, FAME generated and total process achive in the experiment with methanol-CO_2 are higher in the experiments with the CO_2 was used as co-solvent.

At 4.13 ml/min, temperature of extraction of 314 K, temperature of reaction 473 k , 10 MPa and 27% (v/v) of CO_2 in the solvent was achive 97% of oil extracted, 87% of FAME generated and a total process yield of 86%. Results of 93% for oil extracted, between 48-64% for FAME generated and between 44-60% for the total process, were obtained using pure methanol between 3- 5 ml/min at 573.15 K and 10MPa. The use of CO_2 as co-solvent allows to work under milder conditions of temperature avoiding possible side reactions, as thermodecomposition of FAME, as well as achieve higher yields of product decreasing the energy consumption in the process.

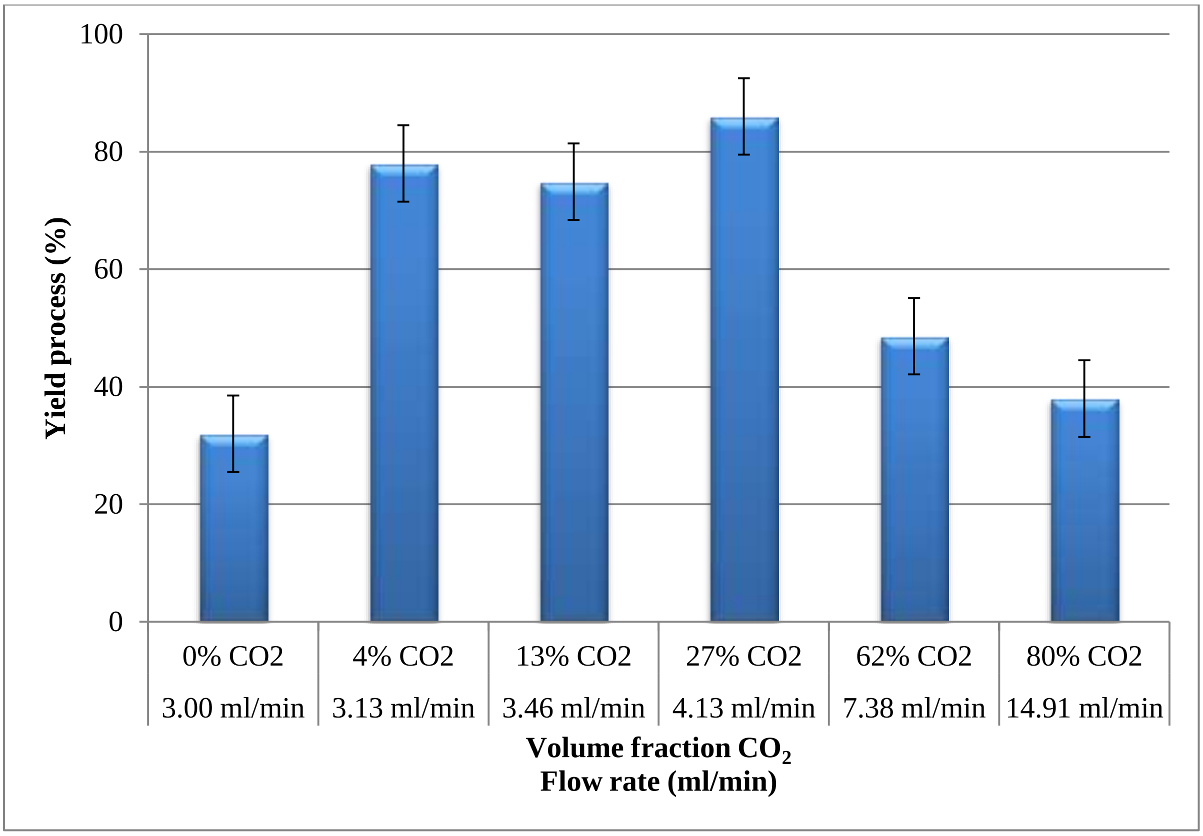


Figure 3.2.3: Influence of the flow rate and volume fraction of CO_2 in the total process yield (%)

3.2.2. Influence of the residence time in the yield of oil extracted (%), FAME (%) and total yield of the process (%)

These experiments were carried out to observe the effect of the residence time in the reactor in the yields of extracted, FAME and total process. To achieve that, it was changed the volume of the reaction section in the installation. Initially in this section had a tube full with small balls of stainless steel to increase the mixing of the flow and reducing the mass transfer limitations (see figure 2.1.2. Model A). Two experiments had been done at same conditions; temperature of extraction section was 313K, temperature of reaction section was 473 K, the pressure of the process was established at 10MPa, the total flow rate was 4.125 ml/min and the volume fraction of CO_2 was 27%. For one of the experiments, the balls inside the reactor tube were removed in order to increase the reaction volume.

The best results were 97% yield of oil extracted, 87% FAME yield and 86% yield for the process with low residence time, see figure 3.2.4. There was not big differences in the values of the two experiments in terms of FAME yield, above 80% of the oil extracted in the two experiments were converted to FAME. At low residence time the 87% of the triglycerides extracted were converted to FAME , and at higher residence times 82% of the triglycerides extracted were converted to FAME, thus indicate that the effect of the reaction time was not too significant in these cases. The little decrease in the values of FAME generated for the experiment with high volume of reaction, could be caused by the absence of the small stainess steel balls inse the reactor. The effect of the balls into the reactor is to increase the mixing between the solvent and the solute. So it was preferable to maintain the mixing effect in ordet ot achieve higher FAME yields than increase the residence time inside the reactor.

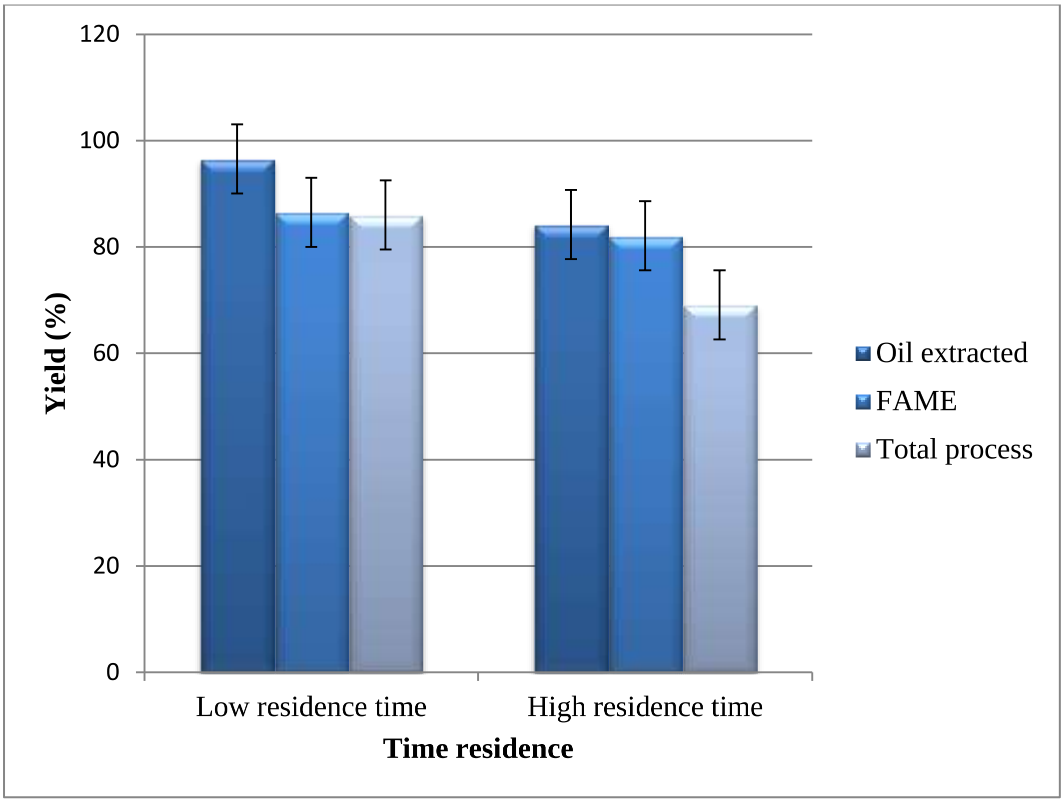


Figure 3.2.4: Influence of residence time in the yield of oil extracted (%), FAME yield (%) and total process yield (%)

3.2.3. Influence of the configuration of the installation in the yield of oil extracted (%), FAME (%) and total yield of the process (%)

After some modifications in the instalation system, it was possible to test the original configuration, direct extraction and reaction, for the process using CO_2 as co-solvent (see figure 2.1.2, Model B). The principal change made to the installation was at zone of the recovery of the samples. Initially, the recovery of the samples took place after the BPR valve, in a vial inmersed an ice bath, to avoid the evaporation of the methanol into the atmosphere. When the experiments with CO_2 were realized, it was observed that some amounts of samples were lost at the recovery of the experiments, principally working with high flow rates of methanol and CO_2. When the flow rates were high , CO_2 came out of the installation at high velocity and some quantities of liquid sample were dragged with it. To avoid this negative effect, it was installed a trap system, immersed in an ice bath. This system allowed to release large quantities of CO_2 without the lost of liquid sample.

In order to study the influence of the configuration of the installation in the efficiency of the process, two types of configurations at the same conditions of temperature, pressure, total flow ratio and volume fraction of CO_2 were tested. Temperature of extraction was 314.15 K, temperature of reaction was 473.15 K, pressure of the system was 10MPa, total volume flow rate was 13.27 ml/min and volume fraction of CO_2 of 80%. It had to be selected a high value for the flow rate in order to allow operate with mixtures of methanol- CO2 in that type of configuration of the installation. At low values of flow rate, the experiments realized were not representative.

The best results correspond to direct extraction/reaction configuration, with a extraction yield of 80%, FAME yield of 65% and the yield of the total process of 52%, as the nex figure shows:

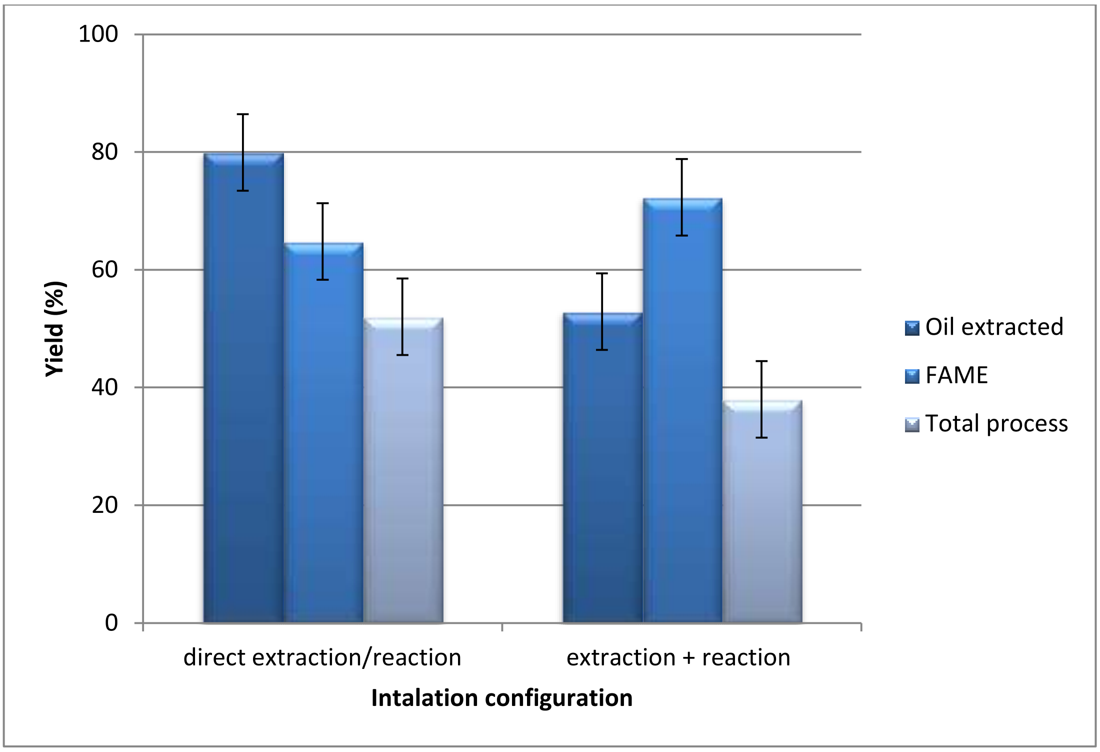


Figure 3.2.5: Influence of the configuration of the installation in the yield of oil extracted (%), FAME yield (%) and yield (%) of the total process

In the case of the direct extraction/reaction, the amount of TG extracted form the SCG was the highest, 80%, but the yield of the reaction into FAME presented a value of 65%, lower than the value of 72% of FAME yield for the extraction+ reaction configuration. The product from the extraction+ reaction configuration presented best purity but it was obtained in less quantity than the product from the direct extraction/ reaction configuration.

The results indicate that the best configuration to work with, in both methanol and mixtures of methanol- CO_2 cases, is the direct extraction /reaction configuration. However it is necessary to optimize some aspects of the installation, principally the separation section.

CHAPTER 4: CONCLUSIONS

The catalyst free production of biodiesel via direct transesterification in continuous mode has proved to be a high potential process for both type of process proposed; direct tranesterification with supercritical methanol and direct tranesterification with supercritical methanol- CO_2 mixtures.

The best result for transesterification reaction with supercritical methanol was obtained at 533 K, 10 MPa and a flow rate of methanol of 1 ml/min. Total process yield was 83%, the yield of TG extracted was 95% and FAME yield correspond to 87%.

The use of methanol/CO_2 mixtures in the transesterification process presented higher yields in oil extraction, 97%, FAME generation, 87%, as well as total process yield, 87%, in milder conditions of temperature. The temperature of the extraction was 314 K, the temperature of the reaction was 473K, 10 MPa and 4.13 ml/min flow rate. This results indicates that the use of a co-solvent like CO_2 increase the efficiency of the process, achieving high quantities of product with more purity, and reducing the energy consumption.

Although we can conclude that the process decribed in this work is a high potencial process, some technical aspects still need to be fine tuned.

The major problem associated to this process was related with the stability of the temperature along the installation. Even though the heat controllers had been programed in order to achieve a high reproducibility between experiments, that proved to be sometimes difficult with some temperature variation between experiments, and interfered both in the efficiency of the extraction/reaction process. Close to the critical point the density of the solvent can drop sharply with slight increases of temperature.

Another problem that needs to be addressed in the future is in the sample recovery. After the BPR valve a trap system inserted in an ice bath was installed in order to avoid the evaporation of the methanol into the atmosphere, nevertheless still high amounts of the sample were not recovered and lost into the atmosphere .

The reaction step shoud be characterized individually by using oil previously extracted from the SCG and supercritical methanol, with and without the use of $ScCO_2$ as co-solvent. It would be interesting to explore the kinetics of the reaction as function of the conditions of pressure and temperature.

APPENDIX A

Table A I: Specifications of EN 14105 comparing to conventional Diesel

PROPERTIES	DIESEL	BIODIESEL
Density 288 K	0.82-0.86	0.86-0.9
Viscosity 313 K	2.0-4.5	3.5-5.0
Flash Point (K)	>377	>423
Sulfur (% mass)	<0.2	<0.01
Sulphated ash (5 mass)	<0.01	0.02
Water (mg/kg)	<200	<500
Carbon residues (% weigh)	<0.03	<0.03
Total contamination (mg/kg)	-	<24
Copper corrosion (3h/323 K)	Class I	Class I
Cetane number	>45	>51
Methanol (% mass)	-	<0.2
Ester content (% mass)	-	>0.95
Monoglycerides content (% mass)	-	<0.8
Diglycerides content (% mass)	-	<0.2
Triglycrides content (% mass)	-	<0.4
Free glycerin (% mass)	-	<0.02
Total glycerin (% mass)	-	<0.25
Iodine number	-	120
Phosphorous (mg/kg)	-	<10
Alkaline metals Na, K (mg/kg)	-	<5
Methyl esters of linolenic acid (% mass)	-	<12
Mehyl esters polyunsaturated (≥4 double bonds) (% mass)	-	<1

APENDIX B

Table B I: Description of the fatty acid profile in vegetable oils.

SATURATED		
Fatty acid	**Symbol**	**Molecule formula**
Lauric acid	C12:0	$C_{12}H_{24}O_2$
Palmitic acid	C16:0	$C_{16}H_{32}O_2$
Stearic acid	C18:0	$C_{18}H_{36}O_2$
UNSATURATED		
Fatty acid	**Symbol**	**Molecule formula**
Oleic acid	C18:1	$C_{18}H_{34}O_2$
Linoleic acid	C18:2	$C_{18}H_{32}O_2$
Linolenic acid	C18:3	$C_{18}H_{30}O_2$

APENDIX C

❖ SAMPLE PREPARATION

The solvent used was n-Heptane and the internal standards used were IS1 (Butan-Triol) and IS2 (Tricaprin) respectively. The derivative agent is MTSF (N-Methyl-N-trimethylsilyltrifluoroacetamide) .The concentrations of internal standards, derivative agent and solvent depend from sample to sample, because the amount of dry sample in each sample is different. A vial with the amount of dry sample was weighed and there was added the amounts of IS1, IS2, derivative agent MTSF, in this proportions:

For each mg of sample, were added:

- 0.8 µl IS1
- 1 µl IS2
- 1 µl MSTFA
- And after 15 minutes, there was added 80 µl of n-Heptane for each mg of dry sample.

An amount of 1.5 ml of each sample with the internal standards and the solvent was transferred to a GC-vial. After that, vial was already prepared to be injected.

APENDIX D

❖ CALIBRATION CURVES

Here, it is shown the calibration curves used to analyze the methyl esters and triglycerides in the various experimental runs. The internal standards used were: triolein, diolein, monolein and glycerol

From the calibration standard, a relationship between the sample concentration and the peak area can be determinate.

$$\frac{[TRIGLYCERIDE]}{[INTERNAL\ STANDARD\ ]} = RF \times \frac{AREA\ Triglyceride}{AREA\ Internal\ Standar} + Kp$$

Equation D.I: Calculation of the concentration of triglycerides

$$\frac{[DIGLYCERIDE]}{[INTERNAL\ STANDARD\ ]} = RF \times \frac{AREA\ Diglyceride}{AREA\ Internal\ Standar} + Kp$$

Equation D.II: Calculation of the concentration of diglycerides

$$\frac{[MONOGLYCERIDE]}{[INTERNAL\ STANDARD\ ]} = RF \times \frac{AREA\ Monoglyceride}{AREA\ Internal\ Standar} + Kp$$

Equation D.III: Calculation of the concentration of monoglycerides

$$\frac{[GLYCERIN]}{[INTERNAL\ STANDARD\ ]} = RF \times \frac{AREA\ Glycerin}{AREA\ Internal\ Standar} + Kp$$

Equation D.IV: Calculation of the concentration of glycerin

Graphically,

$$\frac{[TRIGLYCERIDE]}{[INTERNAL\ STANDARD\ ]}\ vs\ \frac{AREA\ Triglyceride}{AREA\ Internal\ Standar}$$

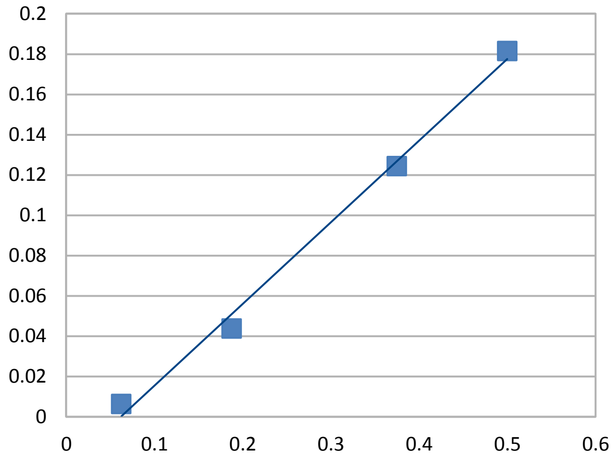
$$\frac{[DIGLYCERIDE]}{[INTERNAL\ STANDARD\ ]}\ vs\ \frac{AREA\ Diglyceride}{AREA\ Internal\ Standar}$$

$$\frac{[MONOGLYCERIDE]}{[INTERNAL\ STANDARD\ ]}\ vs\ \frac{AREA\ Monoglyceride}{AREA\ Internal\ Standar}$$

$$\frac{[GLYCERIN]}{[INTERNAL\ STANDARD\ ]}\ vs\ \frac{AREA\ Glycerin}{AREA\ Internal\ Standar}$$

It is possible to get the calibration standard with the response factor given by ***m*** value from the graphic representation.

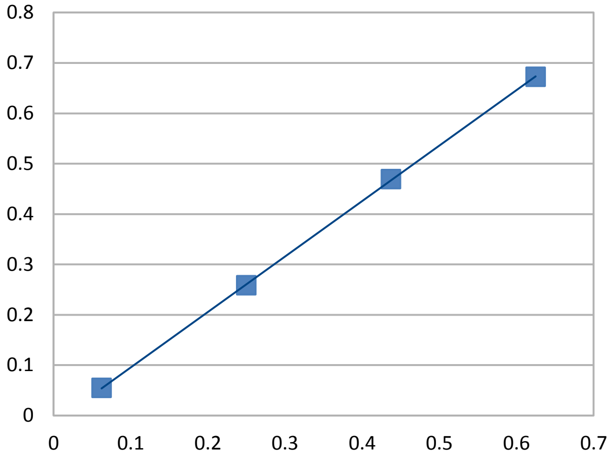
Triolein



$$y = 0.4048\ x + 0.0249$$

$$r^2 = 0.99941$$

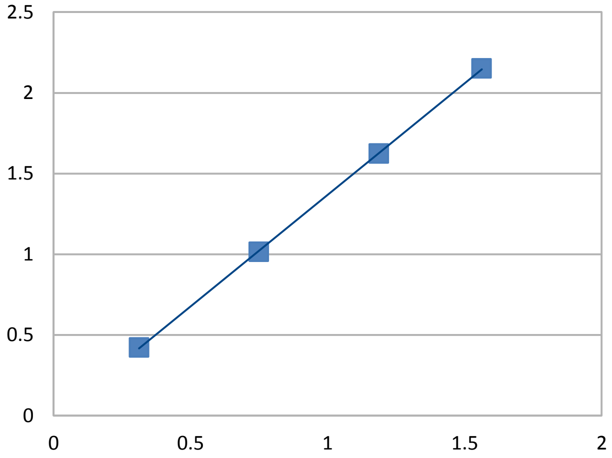
Diolein



y = 1.1002 x – 0.0145

$r^2 = 1$

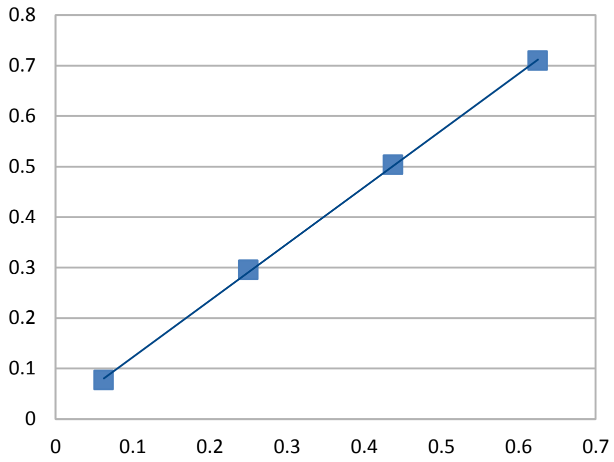
Monolein



y = 1.383 x – 0.0154

$r_2 = 0.9999$

Glycerol



$$y = 1.1225\,x + 0.0105$$

$$r^2 = 0.9998$$

Four solutions were previously prepared with known concentrations and then injected. The method for the results analysis is described in EN 14105.

APENDIX E

- **VOLUME FRACTION CO_2/MeOH**

Table E I: Isobaric properties of methanol at 10 MPa[1]

Temperature (K)	Pressure (MPa)	Density (g/ml)	Phase
288	10	0.80452	liquid
289	10	0.80363	liquid
290	10	0.80274	liquid
291	10	0.80185	liquid
292	10	0.80096	liquid
293	**10**	**0.80007**	**liquid**
294	10	0.79918	liquid
295	10	0.79829	liquid
296	10	0.79740	liquid
297	10	0.79651	liquid
298	10	0.79562	liquid

Table E II: Isobaric properties of CO_2 at 10 MPa[1]

Temperature (K)	Pressure (MPa)	Density (g/ml)	Phase
268	10	0.99825	liquid
269	10	0.99352	liquid
270	10	0.98874	liquid
271	10	0.98390	liquid
272	10	0.97901	liquid
273	**10**	**0.97405**	**liquid**
274	10	0.96903	liquid
275	10	0.96394	liquid
276	10	0.95879	liquid
277	10	0.95356	liquid
278	10	0.94825	liquid

Table E III: Isobaric properties of methanol at 20 MPa[1]

Temperature (K)	Pressure (MPa)	Density (g/ml)	Phase
288	20	0.81262	liquid
289	20	0.81177	liquid
290	20	0.81092	liquid
291	20	0.81006	liquid
292	20	0.80921	liquid
293	20	0.80836	liquid
294	20	0.80751	liquid
295	20	0.8066	liquid
296	20	0.80581	liquid
297	20	0.80496	liquid
298	20	0.80411	liquid

Table E IV: Isobaric properties of CO_2 at 20 MPa[1]

Temperature (K)	Pressure (MPa)	Density (g/ml)	Phase
268	20	1.0398	liquid
269	20	1.0959	liquid
270	20	1.0321	liquid
271	20	1.0283	liquid
272	20	1.0244	liquid
273	20	1.0205	liquid
274	20	1.0166	liquid
275	20	1.0126	liquid
276	20	1.0087	liquid
277	20	1.0047	liquid
278	20	1.007	liquid

M_{MeOH}= 32 g/ mol

M_{CO2}= 44 g/ mol

Volume Flow (MeOH) = 3 ml/ min

Volume Flow (CO_2) = 11.32 ml/min for a volume fraction CO_2= 0.76 (v/v)

$$Volume\ fraction\ CO2\ /MeOH = \frac{Volume\ flow\ rate\ CO2}{Volume\ flow\ rate\ CO2 + Volume\ flow\ rate\ MeOH}$$

Equation E I: Volume fraction of CO_2

The temperatures considered for the calculations of molar ratios were 293 K and 273 K for the MeOH and CO_2 respectively. It was considered these temperatures because these were verified, in the average, in most experiments.

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[1] Source: webbock.nist.go

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