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The Role of Additives for Diesel and Diesel Blended (Ethanol or Biodiesel) Fuels: A Review

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Around the world, there is a growing increase in biofuels consumption, mainly ethanol and biodiesel as well as their blends with diesel that reduce the cost impact of biofuels while retaining some of the advantages of the biofuels. This increase is due to several factors like decreasing the dependence on imported petroleum; providing a market for the excess production of vegetable oils and animal fats; using renewable and biodegradable fuels; reducing global warming due to its closed carbon cycle by CO_2 recycling; increasing lubricity; and reducing substantially the exhaust emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from diesel engines. However, there are major drawbacks in the use of biofuel blends as NOx tends to be higher, the intervals of motor parts replacement such as fuel filters are reduced and degradation by chronic exposure of varnish deposits in fuel tanks and fuel lines, paint, concrete, and paving occurs as some materials are incompatible. Here, fuel additives become indispensable tools not only to decrease these drawbacks but also to produce specified products that meet international and regional standards like EN 14214, ASTM D 6751, and DIN EN 14214, allowing the fuels trade to take place. Additives improve ignition and combustion efficiency, stabilize fuel mixtures, protect the motor from abrasion and wax deposition, and reduce pollutant emissions, among other features. Two basic trends are becoming more relevant: the progressive reduction of sulfur content and the increased use of biofuels. Several additives' compositions may be used as long as they keep the basic chemical functions that are active.

1. Overview

According to the World Trade Organization, in 2004, the fuel market was responsible for an 11.1% share of the total trade in merchandising and primary products, corresponding to 48.1 billion dollars. Most is due to diesel that is essential for transport and heavy-duty engines. It contributes to the prosperity of the worldwide economy since it is widely used due to high combustion efficiency, reliability, adaptability and cost-effectiveness. However, pollutant emissions are a major drawback.

Emissions from diesel engines seriously threaten the environment and are considered one of the major sources of air pollution. It was proved that these pollutants cause impacts in the ecological systems, lead to environmental problems, and carry carcinogenic components that significantly endanger the health of human beings. They can cause serious health problems, especially respiratory and cardiovascular problems. Increasing worldwide concern about combustion-related pollutants, such as particulate matter (PM), oxides of nitrogen (NOx), carbon monoxide (CO), total hydrocarbons (THC), acid rain, and photochemical smog and depletion of the ozone layer has led several countries to regulate emissions and give directives for implementation and compliance. It is commonly accepted that clean combustion of diesel engines can be fulfilled only if engine development is coupled with diesel fuel reformulation or additive introduction.[1,2] In this way, methods to reduce PM and

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NOx emissions include high-pressure injection, turbocharging, and exhaust after treatments or the use of fuel additives, which is thought to be one of the most attractive solutions.[3−5]

Engine exhaust contains volatile organic compounds (VOCs), which embody unburned fuel emissions and other VOCs generated as byproducts of incomplete combustion (PIC). Some VOCs described as being of health concern are acetaldehyde, acrolein, benzene, 1,3-butadiene, formaldehyde, and naphthalene. Gasoline- and diesel-powered vehicles are the largest source of VOCs in most urban areas.[5]

Diesel oil is a fuel derived from petroleum and consists mainly of aliphatic hydrocarbons containing 8−28 carbon atoms with boiling points in the range of 130−370 °C. It is a blend of fractions of hydrocarbons heavier than those of the hydrocarbons in gasoline and with a lower H/C mass ratio, which determines the high emission of carbon compounds per unit of energy delivered to the engine. A reduction in consumption and improvements in the quality of diesel oil have been the object of study by various specialists, motivated by growing demands in the transport and electric sectors.

Commercially available diesel oil is a combination of fossil diesel and several additives, which are added in several amounts to perform specific functions. Among others, there are additives to (1) reduce pernicious emissions; (2) improve fluid stability over a wider range of conditions; (3) improve the viscosity index, reducing the rate of viscosity change with temperature; (4) improve ignition by reducing its delay time, flash point, and so forth; and (5) reduce wear with agents that adsorb onto metal surfaces and sacrificially provide chemical-to-chemical contact rather than metal-to-metal contact under high-load conditions.

There is also an increasing trend to use blends with biomass products such as vegetable oil, ethanol, and biodiesel by increasing the use of alternative fuels. Blends of diesel and biodiesel usually require additives to improve the lubricity, stability, and combustion efficiency by increasing the cetane number. Blends of diesel and ethanol (E-diesel) usually require additives to improve miscibility and reduce knock.

Diesel additives can also be classified according to the purpose for which they are designed. Preflame additives are designed to correct problems that occur prior to burning and include dispersants, pour point depressants, and emulsifiers, which act as cleaning agents. Flame additives are used to improve combustion efficiency in the combustion chamber, to increase cetane number, to reduce the formation of carbon deposits, to avoid oxidation reactions and contamination of fuel and filters clogging by rust, and to inhibit potential explosions caused by changes in static electricity.[6] Postflame additives are designed to reduce carbon deposits in the engine, smoke, and emissions.[7]

2. Types of Additives

2.1. Metal-Based Additives. Some metal-based additives are reported to be effective in lowering diesel emissions. They may reduce diesel emissions by two ways. First, the metals either react with water to produce hydroxyl radicals, which enhance soot oxidation, or react directly with carbon atoms in the soot, thereby lowering the oxidation temperature.[7−9] When these additives are used after combustion in the engine, the metal acts as a nucleus for soot deposition. Usually, the additive is added as a metal-organic compound, and it is emitted in the particulate phase as oxide, on soot particles or forming new nanometer-sized particles by homogeneous nucleation of the additive.[10,11]

Particle traps are suitable tools for minimizing soot emissions.[12] However, a technical challenge is the regeneration of clogged filters because online regeneration demands a minimum temperature of 550 °C and an oxygen content of 5%, which cannot be attained without additional burners or catalytic combustion. The principle of this additive action consists of a catalytic effect on the combustion of hydrocarbons. Transition or noble metals (e.g., Ce, Fe, Cu, Sr, or Pt) in the form of fuel additives or coatings can substantially lower the soot ignition temperature.[1] A large variety of metal additives have been investigated. Some examples are a catalytic phase based on eutectic mixtures of Cs_2O, V_2O_5, and MoO_3;[13] succinimide dispersant; calcium alkylsulfonate and zinc dithiophosphate;[14] additive Mg-based[15] compounds based on Mg, Ca, Mn, and Cu;[4] ferrocene;[8] Ce-, Cu-, and Fe-based additives;[11] and a Ce additive.[12]

A serious problem associated with diesel emissions is the presence of polycyclic aromatic hydrocarbons (PAHs). Several PAHs are known to be mutagenic and/or potentially carcinogenic toward humans.[5] Manganese-based additives have been used to investigate the effects on PAH emissions. Yang et al. showed that Mn-based additives might reduce the emission of regulated pollutants (PM, CO, HC, and NOx) as well as unregulated pollutants (PAHs).[7] By adding 400 mg/kg of Mn-based additive into the diesel fuel, the mean reduction fraction of the mean total PAH emission was 37.2%, while for the 10 higher molecular weight PAHs, the mean reduction fraction was 64.5%. These results indicate that Mn-based additives in diesel engines can act as catalysts enhancing the oxidation process and reducing a considerable amount of PAH emission.[7] Particles smaller than 50 nm are more abundant during the use of these additives, and the total particle number concentration can even be larger. No PAHs or elemental carbon is detectable in the particle fraction below a 50 nm diameter.[16] The freezing point is affected when Mn-based additives are used. There is a linear relation between lower dosages of additives and reduction of the freezing point. This is attributed to Mn compounds' effects on fuel colligative properties, and a stronger attraction effect occurs between the ions when the concentration is increased. Güru et al. showed that cetane number, CO_2, and net efficiency were increased and CO and SO_2 were decreased when Mn additives were added to the diesel fuel. The reduction in SO_2 is explained by the formation of $MnSO_4$.[4]

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In studying ferrocene additives, it was found in particular that they form condensation sites (hypothetically iron oxides) before the formation of carbon particles in the combustion zone. Carbon particles are condensed on them and are totally burned in the following stages of the process.[17] Additionally, ferrocene reduces carbonaceous matter in combustion by more efficient burnout rather than by the inhibition of soot formation. Ferrocene vapor leads to particle formation early in the flame, that is, below the soot inception point of an unseeded flame.[8]

Additives called "smoke suppressants" reduce emissions of black smoke (actually soot) with the exhaust gases from diesel engines. Black smoke is formed in engine overloading and in fuel system malfunctions. Some metal compounds can cause soot to burn, primarily barium, manganese, and calcium compounds, and are proposed as smoke-suppressant additives.[17] A number of workers have investigated the effect of barium fuel additives on carbonaceous particulate (soot) emissions. Barium has been shown to be the most effective of 40 metals tested in reducing carbonaceous particulate emissions. Various investigators have reported 20−75% reductions in visible smoke emissions from diesel exhaust using barium fuel additives.[18]

Other important types of metal-based additives are cerium additives. The cerium additive has a significant effect on reducing the particle emissions.[12] It has been proposed that cerium additives mainly reduce the concentration of organic carbon but not so much the concentration of elemental or black carbon. Elemental carbon is the major constituent when diesel fuels are burned with hydrocarbons and inorganic species. Cerium additives form new particles if concentration of the additive is too high.[12,15] It was observed that the addition of cerium to the diesel fuel decreased the peak number concentrations and the light-off temperature but increased the oxidation rate.[12,17]

The effect of a platinum metal additive on the performance of three metal-based additives for the catalytic oxidation of diesel particulate was studied, and the results showed that, especially, a combination of platinum and cerium additives is very active in the catalytic oxidation of diesel particulates. The additive dose rate can be very low, that is, about 5 ppm cerium and 0.25 ppm platinum, without a loss of effectiveness. NO_2 plays a key role in this process. Platinum accumulated on the filter catalyzes the oxidation of NO to NO_2, whereas cerium catalyzes the oxidation of particulate with NO_2. Copper and iron do not catalyze the latter reaction. An additional effect of this oxidation mechanism is a substantial NO_2 reduction.[19]

2.2. Oxygenated Additives. Another group of fuel additives is oxygenated compounds. The idea of using oxygen to produce a cleaner burning of diesel fuels is half a century old.[20] Since that early work, numerous researchers have reported the addition of a variety of oxygenated compounds to diesel fuel. Some oxygenate compounds used are ethanol,[2,21−23] acetoacetic esters and dicarboxylic acid esters,[24] ethylene glycol monoacetate,[25] 2-hydroxy-ethyl esters,[26] diethylene glycol dimethyl ether, sorbitan monooleate and polyoxyethylene sorbitan monooleate,[27] dibutyl maleate and tripropylene glycol monomethyl ether,[28] ethanol and dimethyl ether,[20] dimethyl ether (DME), dimethyl carbonate (DMC) and dimethoxy methane,[3] 1-octylamino-3-octyloxy-2-propanol and N-octyl nitramine,[21] dimethoxy propane and dimethoxy ethane,[29] biodiesel,[22,30,31] and a mixture of methanol and ethanol.[6]

Oxygenated additives have been considered for reducing the ignition temperature of particulates. However, the reduction of particulate emissions through the introduction of oxygenated compounds depends on the molecular structure and oxygen content of the fuel[32] and also depends on the local oxygen concentration in the fuel plume. To reduce particulate emissions, fuel-compatible oxygen-bearing compounds should be blended with diesel to produce a composite fuel containing 10−25% v/v of oxygenate.[28] Therefore, the composition of diesel and the use of additives directly affect properties such as density, viscosity, volatility, behavior at low temperatures, and the cetane number.[2,4,20,22,24,25,31,33−35] Zabetta et al. showed that the ignition temperature of particulates from seed-derived oils (SO) and from blends of SO with diesel fuel (DO) can be lower than that of particulate from neat DO.

According to de Menezes et al.,[33] by increasing the concentration of additives (e.g., ethanol and ethyl tert-butyl ether or tert-amyl ethyl ether), there is a reduction in the cetane number, and an increase in hydrocarbons leads to a decrease of CO up to 20% in relation to diesel fuel alone. The fuel cetane number decreases with an increase of ethanol content in the fuel because of the low cetane number of this alcohol. Another factor that influences the decrease in cetane number level is the incomplete combustion of the ethanol−air mixture. Factors causing combustion deterioration, such as high latent heats of evaporation, could be responsible for the increased CO emission. Another reason for the high CO emission is the increase in ignition delay. This leads to a lower combustion temperature at lower and medium loads.[6,22,23] NOx emissions decrease with ethanol addition.[23] In addition, a measurable increase of the concentration of oxygen in combustion products from the blends was observed. This may be another cause of the NOx increase.[22,36]

The presence of some oxygenated additives (ethanol, 1-octylamino-3-octyloxy-2-propanol, and N-octyl nitramine) results in the formation of a lubricant film with beneficial antiwear properties. The increase volatility of the mixture is also apparent as a lower flash point at ambient temperature. Although this does not have a direct effect on engine performance, such mixtures would be subject to the legislation concerning fuel handling.[2,21,22,36]

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DME is a potential ultraclean diesel fuel. Dimethyl ether burns without producing the smoke associated with diesel combustion and can be manufactured from synthesis gas or methanol. However, DME has a low viscosity compared to diesel fuel and has insufficient lubricity to prevent excessive wear in fuel injection systems. A strategy in order to obtain cleaner-burning fuels with satisfactory properties is the use of diesel−DME blends. The viscosity of blends of DME with various fuels and additives, including low-sulfur diesel fuel, soybean oil, biodiesel, and various lubricity additives, was characterized over a range of blend ratios. It was observed that none of the additives or fuels provides adequate viscosity when blended with more than 50% DME. Viscosity, rather than lubricity, may be the limiting factor in using DME.[37] Song et al. affirmed that there are conflicting results regarding the effect of the structure of an oxygenated compound blended with diesel on the level of reduction of the particulate emissions.[20] They concluded that DME was still more effective than ethanol in reducing aromatic species.

Diesel fuels with a low sulfur content are characterized by poor antiwear properties. It is believed that, when the sulfur content in the fuel is less than 0.05%, special antiwear additives should be used. The most common additives of this type contain carboxylic acid derivatives: esters, amides, products of the transesterification of vegetable oils and animal fats with alcohols or phenols, hydrocarbons with several polar functional groups, amino groups, or hydroxyls, for example.[17]

Ethylene glycol monoacetate was found to be a promising candidate as an oxygenated diesel additive due to its low-poison and oxygen-rich composition properties. Experimental results showed that increasing the ethylene glycol monoacetate ratio in diesel fuel caused an increase in the brake-specific fuel consumption while the excess air and oxygen emission concentrations decreased.[25]

The 2-methoxyethyl acetate (MEA) can be easily blended with diesel, with little change in the fuel delivery system, engine power, and fuel consumption. Experiments showed that MEA was a good oxygenated additive of diesel for compression-ignition engines and can be used to decrease emissions of smoke, HC, and CO (Yanfeng et al., in press). Other environmentally safe additives for diesel fuels were tested: high-molecular-weight monohydric, dihydric, trihydric, and tetrahydric alcohols; carboxylic and polycarboxylic acids; $C_{24}-C_{65}$ mono- or polycarboxylic acid esters with two to three carboxyl groups and C_2-C_9 multihydric alcohols with 2−10 hydroxyl groups; mixtures of synthetic or plant esters of mono-, di-, tri-, and tetrahydric C_2-C_{18} alcohols and carboxylic acids with C_3-C_{45} acyls; the product of the reaction of aromatic triazole (tolyltriazole) and a $C_{10}-C_{40}$ fatty acid; and so forth. The studies showed the weak effect of the additive compounds containing carbonyl, ether, and ester groups on the antiwear properties of the fuel. The following compounds are in ascending order with respect to antiwear effectiveness: ethers, aldehydes and ketones, esters, alcohols, and acids.[38]

DMC is usually used as an oxygenated additive to improve combustion and reduce emissions of diesel engines.[39] Dimethyl carbonate presents good blend fuel properties and reduces smoke almost linearly with its concentration. However, it is difficult to fuel diesel engines directly with DMC due to its low cetane number and high latent heat of vaporization. The addition of 10% dimethyl carbonate in the fuel promotes a smoke reduction of 35−50%, and also apparent reductions of hydrocarbons and carbon monoxide densities were attained with a slight increase in NOx emissions. The engine fueled with dimethyl carbonate emitted almost smokeless exhaust gas because this oxygenated fuel has no C═C bonds in the molecules. To study DMC combustion in diesel engines, Xiaolu et al. proposed an approach that combines internal exhaust gas recirculation with a small injection of diesel fuel to ignite the DMC.[40] Preliminary studies demonstrated that this engine can be fueled with DMC with an almost zero level of smoke and a low exhaust gas temperature. This DMC-fueled engine has lower NOx emissions and 2−3% higher effective thermal efficiency than the engine operated with diesel in moderate and high load zones.

The chemical agent diglyme, which is used as an oxygenated additive to diesel fuel, improves combustion characteristics of diesel engines, boilers, and furnaces. The emulsification properties of a multiphase emulsion of the oil-in-water-in-oil (O/W/O) type added with this oxygenated agent were investigated by Lin and Wang.[27] Experimental results show that the viscosities of O/W and W/O two-phase emulsions increase with an increase of their inner phase content and the addition of diglyme. The addition of a diglyme agent to the emulsions deteriorates the emulsification activity and emulsification stability of W/O and O/W/O.

2.3. Depressants and Wax Dispersants. Petroleum distillate fuels contain *n*-paraffin waxes that tend to be separated from the oil at low temperatures. The waxes generally crystallize as an interlocking network of fine sheets, thereby trapping the remaining fuel in cagelike structures and causing cold-flow problems such as clogging of fuel lines and filters in engine fuel systems. Several techniques have been used to minimize the problems caused by the wax deposition, and the continuous addition of polymeric inhibitors is considered to be an attractive technological alternative. The addition of copolymers such as polyacrylates, polymethacrylates, or poly(ethylene-*co*-vinyl acetate) (EVA) inhibits the deposition phenomenon; those copolymers are composed of a hydrocarbon chain, which provides the interaction between additives and paraffin, and a polar segment that is responsible for the wax crystal morphology modification necessary to inhibit the aggregation stage. Those copolymers are known as cold-filter plugging point (CFPP) additives or pour point depressants (PPDs). EVA copolymers present a good efficiency as diesel fuel CFPP additives.[41]

The addition of PPDs has been proved to be an efficient way to inhibit the wax deposition of diesel fuels. However, the complexity of the oil is far beyond current commercial PPD products. So far, it mainly depends on syntheses of numerous candidate compounds followed by repeating experimental measurements in order to improve the efficiency of PPDs. Wu et al. used molecular dynamic simulation to investigate the interaction between crystal planes of wax and EVA, as well as its derivatives with different branches, on the basis of the model of wax.[42] Side-chain effects on adsorption energy and equilibrium adsorption conformations were studied under different kinds and numbers of branches. They concluded that side chains introduced by propylene were a benefit to the affinity between the EVA-type molecules and alkanes in the wax plane, comparing with those branches introduced by butylenes. Molecular

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dynamic simulation calculations indicated that EVAP with one branch adjacent to the VA (vinyl acetate) group would be a better PPD additive than EVA in diesel fuels.[42]

Wax dispersant additives are especially important in countries with long winters. It was shown that traditional depressants (polyacrylates and copolymers of olefins and vinyl acetate) do not prevent separation during cold storage by reducing the solid point of the fuels. As a result, the fuel separates into two layers: an upper, clear layer and a lower, cloudy layer rich in waxes. Both layers are mobile, but when fuel is taken off of the lower layer, the engine misses. Special additives—wax dispersants or precipitators—solve the problem. Their effect consists in the formation of very small wax crystals with high sedimentation stability. They are acid amides, polymers modified with amino groups, and so forth.[43]

The high freezing point of diesel fuel causes clogging of filters, and hence, there are some difficulties when it is used in cold conditions. In order to reduce the freezing point of the fuel, about 100 ppm of paradine is added, commonly after refining.[4] The mechanism of action of additives that control the sedimentation of paraffin crystals after their crystallization in model diesel oil has been studied by Marie et al.[43] The chemical analysis of the crystals and detailed measurements of the sedimentation phenomenon give new insights into this complex process. Thus, the wax antisettling additives used for preventing wax crystal sedimentation adsorb onto surfaces of wax particles and provide them with enhanced colloidal stability. The settling rate is not related to the size of the crystals or to the viscosity of the liquid medium, but to the ability of the additives to prevent the aggregation of wax crystals.

2.4. Ignition Promoters. In internal combustion engines operating on diesel fuel, the cetane number of the fuel is one of the most important characteristics of the combustion process. Improved ignition is detected as a decrease in the ignition delay time, the ignition delay time being measured as the time between the start of fuel injection and detectable ignition. Shorter ignition delay times have been directly correlated with a faster startup in cold weather, reduced NOx emissions, and smoother engine operation.[44] This parameter is a function of the composition and the structure of the hydrocarbons present in the diesel. It decreases with an increase in the aromatic hydrocarbon content and increases with an increase in the *n*-paraffin and olefin content.[45] The utilization of cetane-improving additives is necessary to avoid difficulties in cold starting and other performance problems associated with low cetane numbers. Ignition promoters have traditionally been given to alkyl nitrates (e.g., amyl nitrate, hexyl nitrate, and octyl nitrate), but azo compounds and alkyl peroxides have also been proposed.[17,46]

The commercial market considers several factors when selecting and using cetane improvers; these include (a) efficacy toward improving ignition properties, (b) hazards associated with storage and transport, (c) additional costs associated with diluting cetane improvers to allow safe transport, and (d) nitrogen content.[44]

Alkyl nitrates are characterized by relatively high efficiency and, simultaneously, many serious drawbacks. They are toxic and corrosive and worsen the color of the fuels during storage. For this reason, the attempts to create ignition promoters based on other compounds are ongoing, and organic peroxides have received the most attention. Among the organic peroxides, symmetric dialkyl and diaryl peroxides are of practical interest. They are more stable in storage and heating and do not decompose on contact with water, olefins, and others compounds which can be present in commercial fuels.[47] In another work, nitrate derivatives of soybean oil were synthesized and evaluated as an alternative to 2-ethylhexyl nitrate (EHN), which currently dominates the cetane improver market. The synthesized additive exhibited NOx-reducing capabilities similar to that of EHN when used in a diesel fuel. They also provided significant lubricity enhancement to the fuels at the same concentrations used to provide the cetane enhancement. Depending on the product, these additives exhibit increased stability and lower volatility than EHN. Commercially competitive enhancements of both ignition-related properties and lubricity were achieved in a single product.[44]

2.5. Diesel−Vegetable Oil Blends. The heating value of vegetable oils is similar to that of diesel fuel. However, their use in direct injection diesel engines is restricted by some unfavorable physical properties, particularly their viscosity. The viscosity of vegetable oil is approximately 10 times higher than that of diesel fuel. Therefore, the use of vegetable oil in direct injection diesel engines creates poor fuel atomization, incomplete combustion, carbon deposition on the injector, and fuel buildup in the lubricant oils, resulting in serious engine fouling. The possible treatments employed to improve the oil viscosity include dilution with a suitable solvent, emulsification, pyrolysis, and transesterification to obtain biodiesel.[48]

Several studies have been conducted using biomass and vegetable oils as alternative fuels or blended with diesel fuel. A study in Indonesia is an example, where palm oil was used as an additive to fuels. A study in which oil was extracted from Pistachia Palestine (PP) fruits is another example. Mixtures of such oil with diesel fuel were tested to determine the potential of the oil as a diesel additive, and successful results were obtained without any engine modifications. It was shown that the addition of PP oil to diesel fuel decreases both the brake power and thermal efficiency of the test engine and increases the brake-specific fuel consumption. This is due to the lower heating value of the PP oil compared to diesel fuel.[49]

Jatropha oil was blended with diesel in a proportion of 2.6% by volume, and it was found that the oil can be used as an ignition-accelerator additive for poor diesel fuels.[50]

Hydroprocessed vegetable oils can be used for diesel fuel improvement as well. In 1996, Canadian researchers investigated the use of conventional refinery technology to convert vegetable oils into a product resembling diesel fuel. It was found that the use of a medium severity refinery hydroprocess yielded a product (“super cetane”) in the diesel boiling range with a high cetane value (55−90) and the impact of the “super cetane”/diesel mixture on engine emissions is similar to the impact cetane enhancement via a nitrate additive when added to conventional diesel fuel. An attractive advantage of hydroprocessing over esterification includes lower processing cost.[51]

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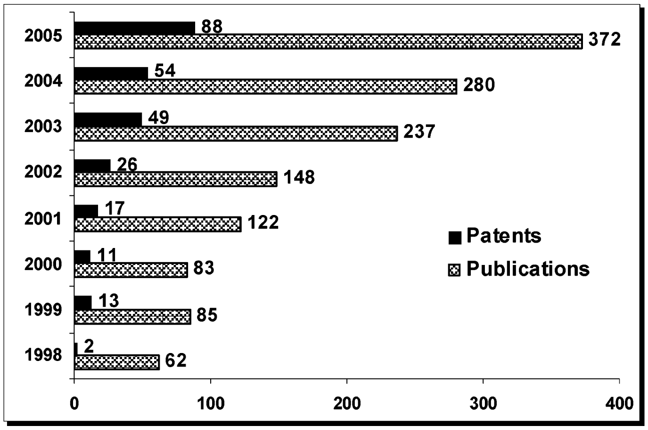

Figure 1. Number of publications and patents about biodiesel in the past few years (Chemical Abstracts database in July of 2006 using <biodiesel> as keyword).

3. Additives for Diesel−Biodiesel Blends

At present, concern about environmental regulations has been the major reason to look for alternative fuels. The use of biodiesel has presented a promising alternative in the world. It is not only a renewable energy source, but it can also reduce the dependence on imported oil and support agricultural subsidies in certain regions.

The growing interest in this renewable fuel could be illustrated by the number of articles and patents published about this issue in the past few years (Figure 1).

Access of the Chemical Abstracts database in July of 2006 using <biodiesel> as a keyword showed that in only the first part of 2006, 286 references were published about this biofuel. These publications focus on several aspects with the aim of making possible the use of biodiesel as fuel. They include appropriate sources of raw material, comparative studies between emissions of diesel and biodiesel, development of new catalysts and new technological routes for the biofuel production, development of qualitative and quantitative methods for its characterization, and so forth. Pinto et al. presented a critical analysis on the most used oil sources, the catalysts and the methods to verify the transesterification yields, and the comparative studies on emissions from fossil diesel and blends with biodiesel in variable proportions.[52] We will approach the use of additives as an alternative to solve some technical problems generated by the use of diesel−biodiesel blends.

3.1. Characteristics of Diesel−Biodiesel Blends versus Diesel. Biodiesel is defined as alkyl esters of fatty acids, obtained by the transesterification of oils or fats, from plants or animals, with short-chain alcohols such as methanol and ethanol. It has an engine performance comparable to that with conventional diesel and could be used pure or blended with diesel.[52,53] Biodiesel is nonflammable, nonexplosive, biodegradable, and nontoxic. Besides, its use provides a reduction of many harmful exhaust emissions. A nearly complete absence of sulfur oxide (SOx) emissions, particulate and soot, and reduction in polycyclic aromatic hydrocarbons emissions can be achieved.

However, there are some technical problems associated with the use of biodiesel fuels. The use of some of them includes an increase in nitrogen oxide (NOx) exhaust emissions, which have stringent environmental regulations, and relatively poor low-temperature flow properties compared to diesel. Another problem is the oxidation stability of biodiesel. The esters of unsaturated fatty acids are unstable with respect to light, catalytic systems and atmospheric oxygen. Since diesel fuels from fossil oil have good oxidation stability, automobile companies have not considered fuel degradation when developing diesel engines and vehicles. It is one of the key issues in using vegetable-oil-based fuels, and attention is given to the stability of biodiesel during storage and use. These problems could be circumvented by using additives.

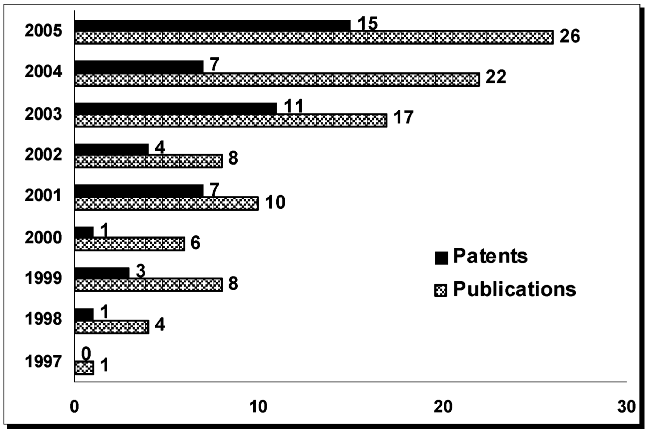

Figure 2. Number of publications about additives for diesel−biodiesel blends (Chemical Abstracts database in July of 2006 using <biodiesel and additives> as keywords).

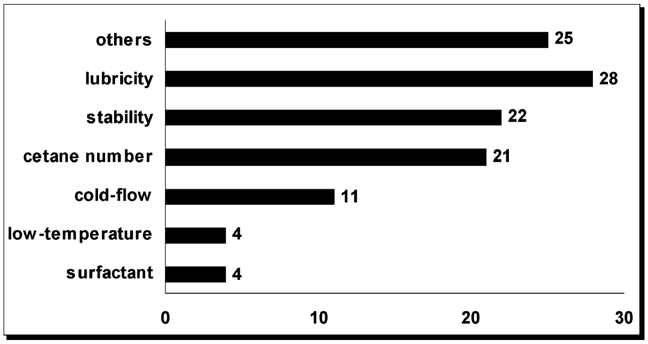

Figure 3. Number of publications by type of additives (Chemical Abstracts database in July of 2006 using <biodiesel and additives> as keywords).

Access to the Chemical Abstracts database in July of 2006 found 1823 references using “biodiesel” as entered. From these, a total of 242 references were found when the refine tool was used with “additive” as a keyword. A careful analysis of the abstracts showed that only 111 references (45.9%), in fact, reported the use of additives for diesel−biodiesel blends. Figure 2 presents the distribution of these references by year.

Figure 2 shows that the number of publications about additives for diesel−biodiesel blends, especially patents, has been increasing in the past few years. The search showed also that lubricity additives are the most studied followed by stability and cetane number additives.

Figure 3 illustrates the number of references by type of additive. Most of the references concern additives for lubricity, cetane number, and stability, which will be focused on in sections 3.2, 3.3, and 3.4, respectively.

There are few studies about additives that can improve the low-temperature performance of diesel−biodiesel blends. The low-temperature properties include the solidification point, pour point, and cold filter plugging point (CFPP). In 2001, a patent

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reported the use of block copolymers of long-chain alkyl methacrylates and acrylates as pour point depressants and flow improvers, suggesting their use as biodiesel fuel additives.[54] Barbour et al. focused on the improvement of cold filter plugging performance in pure biodiesel and diesel−biodiesel blends.[55] Many additives such as ethylene−vinyl acetate copolymers, polymethacrylates, and styrene−maleic anhydride copolymers, allegedly reduce CFPP. Ming et al. studied some additives (synthesized or commercially available) suitable for reducing the pour point and cloud point values of palm oil methyl esters (POME).[56] Among the additives studied in this research were Tween-80, dihydroxy fatty acid (DHFA), acrylated polyester prepolymer, palm-based polyol, a blend of DHFA and palm-based polyol at a 1:1 ratio, an additive synthesized using DHFA and ethyl hexanol, and castor oil ricinoleate. All additives improved the low-temperature properties of biodiesel and presented significant reductions in both the pour point and cloud point of POME.

Cloud points and pour points have been routinely used to characterize the cold flow operability of diesel fuels in the petroleum industry. Cloud points are useful as fuel quality-control specifications for refiners when blending fuels in cold climates and also as low-temperature operability indicators for diesel-powered operators when used at cold ambient temperatures. At the cloud point, long-chain hydrocarbons (or saturated fatty acid ester in biodiesel) begin to form small wax crystals, and when enough wax crystals with diameters exceeding 0.5 mm have precipitated, the fuel appears cloudy. As temperatures decrease below the cloud point, crystals continuously grow and agglomerate until they are large enough to plug fuel filter systems. Eventually, the fuel can gel up and cease to pour even though much of the fuel has not frozen. Pour points are useful for characterizing the suitability of a fuel for wide storage and pipeline distribution.[57] A study reported that blending petroleum diesel with soybean biodiesel could improve its low temperature characteristics. Results showed that blending 20−30% soybean biodiesel with diesel improved the pour point, reducing it by 10 °C.[58]

Surfactants, another class of additives, are used to reduce injector tip deposits. In 2002, a patent reported the use of a product from a succinic acylating agent and a polyamine, having at least one condensable primary amine group, as a surfactant.[59] In 2004, another patent published the use of a salt of a saturated carboxylic acid with an alkylated or alkoxylated amine as an inhibitor of the formation of combustion chamber deposits.[60]

The other 25 references include additives for enhanced postcombustion exhaust gas treatment,[61] substances to lower the crystallization temperature,[62] solubilizers,[63] dispersants,[64] and others. This group of references also includes publications that do not specify the type of additive or just describe general aspects about this issue.

3.2. Lubricity Additives. Fuel lubricity can be enhanced by the addition of lubricity additives. They comprise a range of surface-active chemicals. They have an affinity for metal surfaces, and they form boundary films that prevent metal-to-metal contact that leads to wear under light to moderate loads. Much research shows that the addition of lubricity additives is not necessary in low-sulfur diesel−biodiesel blends once vegetable oil methyl esters enhance the fuel lubricity.[48,65−67] This mixture provides a stable film on the metal surface and substantially reduces the wear scar diameter.[68]

In 1999, Hillion et al. showed that the presence of mono- and diacylglycerols in the range of 100−200 ppm provides sufficient antiwear capacity to safely ensure normal operation of the motor injection system, even when using a low-sulfur diesel.[69] Some years later, Knothe and Steidley compared the lubricity of numerous fatty compounds to that of hydrocarbon compounds found in diesel.[70] According to their study, fatty compounds possess better lubricity than hydrocarbons, because of their polarity-imparting oxygen atoms. Additionally, pure free fatty acids, monoacylglycerols, and glycerol possess better lubricity than pure esters, because of their free OH groups. An order of oxygenated moieties enhancing lubricity (COOH > CHO > OH > $COOCH_3$ > C−O > C−O−C) was obtained from studying various oxygenated C10 compounds. Another experiment, with pure C3 compounds containing OH, NH_2, and SH groups, shows that oxygen enhances lubricity more than nitrogen and sulfur. The addition of biodiesel improves the lubricity of low-sulfur diesel more than pure fatty esters, indicating that other biodiesel components cause lubricity enhancement at low biodiesel blend levels. The addition of polar compounds such as free fatty acids or monoacylglycerols improves the lubricity of low-level blends of esters in low-lubricity diesel. This result suggests that these species, considered as contaminants resulting from biodiesel production, are responsible for the lubricity of low-level blends of biodiesel in low-sulfur diesel. A similar study published by Hu et al. showed that methyl esters and monoacylglycerols determine the lubricity of biodiesel.[71] Free fatty acids and diacylglycerols can also affect the lubricity of biodiesel, but not so much as monoacylglycerols. Triacylglycerols almost have no effect on the lubricity of biodiesel.

In recent years, fatty acid methyl esters (FAMEs), commonly known as biodiesel, have successfully been used as diesel fuel lubricity improvers.[24] The lubricity improvement observed from vegetable-oil-based methyl ester additives is greater than that

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observed when the methyl ester of only one fatty acid is added at the same concentrations. Previous studies have shown that fatty acid esters derived from vegetable oils have increased diesel fuel lubricity at concentrations of less than 1%.[24,30,72] It has been also observed that the fatty acid composition of FAME mixtures may have an impact on their effectiveness as lubricity enhancers. Factors such as saturation, chain length, and hydroxylation could influence the performance of these additives as lubricity enhancers. Oils which contain a high concentration of hydroxylated fatty acids, such as castor oil, produce a FAME mixture with much more effective lubricity than oils that do not contain any hydroxylated fatty acids. The structure of these FAMEs facilitates formation of hydrogen-bonded complexes that enhance the lubricity of mixtures containing these components. The hydroxyl group is significant because it facilitates plasticization and adhesion of the oil esters.[30] When the unsaturation of these FAMEs increased, lubricity enhancement also increased. In the C18 series methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate, methyl linoleate demonstrated the best performance as a lubricity-enhancing additive, and methyl stearate was the least effective.[30] The increase of unsaturation reduces the cetane number, and the increase in chain length increases the cetane number. Besides, increasing the number of double bonds (and their position in the chain) results in a lower cetane number. Branching in the chain is a factor that decreases the cetane number as is shown by use of hexadecane and 2,2,4,4,6,8,8-heptamethylnonane as high- and low-quality standards in the cetane scale.[31] Biodiesel from palm oil when blended with diesel oil in a proportion of 15%, for example, increased brake power and reduced exhaust emissions compared to base diesel.[73]

Additionally, several types of lubricity additives have been proposed. Nonacidic lubricity additives consisting of a mixture of C8-30-hydrocarbyl-substituted succinic anhydrides and an alkanolamine were reported by Henly.[64] Anastopoulos et al. discussed some results, concerning the influence of adding low amounts of specific types of biodiesel, aliphatic amines, tertiary amides, acetoacetates esters, and esters of dicarboxylic acids on the behavior of the steel-on-steel systems, lubricated with low-sulfur diesel fuel.[74] The obtained wear results showed that all the various classes of additives improved fuel lubricity. In another work, biodiesel was produced from four vegetable oils (canola oil, greenseed canola oil from heat-damaged seeds, processed waste fryer grease, and unprocessed waste fryer grease) using methanol and KOH as a catalyst. The methyl esters of the corresponding oils were evaluated to find their diesel additive properties. Results show that, from the four biodiesels produced, the best choice to use as an additive was canola methyl ester, mainly due to the enhancement of the fuel's lubricity number.[48] A beneficial effect on the lubricity of diesel fuel also was observed when biodiesel was produced from rapeseed oil, sunflower oil, corn oil, used fried oil, and olive oil at low concentrations (0.15−0.5% by volume).[74]

Recently, esters of C8−C18 saturated and unsaturated fatty acids produced by the transesterification of vegetable oils with polyhydroxy alcohols have found considerable use as addictives.[75] Suitable polyhydroxy alcohols include neopentyl glycol, trimethylolpropane, trimethylolethane, pentaerythritol, and ethylene glycol.

3.3. Cetane Number Additives. The cetane number measures the readiness of the fuel to autoignite when injected into the engine and is one of the most significant properties to specify the ignition quality of any fuel for internal combustion engines. An increase in cetane number decreases the delay between injection and ignition. One of the more obvious effects of running on a low cetane number fuel is an increase in engine noise. In general, aromatics and alcohols have a low cetane number.[76]

Cetane number value also affects the NOx and particulate matter emissions from diesel, biodiesel, and diesel−biodiesel blend engines, as noted by several authors.[77] A NOx increase results from the advancing injection time of biodiesel and diesel−biodiesel engines as compared to diesel ones.[78−80] A high cetane number leads to a reduction of both emissions, and a lot of studies were carried out to decrease the NOx emission by increasing the cetane number.[34,77,81] Some strategies have been proposed to overcome this effect, such as detection of the presence of biodiesel in the fuel and retarding of the static injection time,[82] or by blending biodiesel with other fuels or additives. McCormick et al. proposed,[77] for instance, a diesel blend consisting of 46% Fischer−Tropsch diesel fuel, a diesel basestock containing 10% aromatics, and a 1 vol % di-tert-butyl peroxide or 0.5 vol % 2-ethyl-hexyl nitrate (EHN). In all cases, the reduction of the NOx emissions came from the increase of the cetane number of the fuel. In addition, Hess et al. studied the effect of antioxidant addition on NOx emissions from an 80% diesel and 20% biodiesel blend and concluded that the 2-EHN additive increased the cetane number of the fuel, leading to a shorter ignition time and thus to a decrease in NOx emissions.[83]

The cetane number of biodiesel ranges from 48 to 67 depending on several parameters such as oil processing technology and climate conditions where the feedstock (vegetable oil) is collected and mainly the fatty acid composition of the base oil.[84] It is well-known that the overall properties of biodiesel are determined by the properties of the several fatty acids which, in turn, depend on the structural features of the fatty acids.[31,77,85] They comprise chain length, unsaturation degree, and branching of the chain. Among these properties, cetane number is especially affected by the structural features of the various fatty esters. The presence of double bonds in fatty acids will lower the cetane number value, and then strategies are addressed to shift the fatty pool of a vegetable oil toward saturated moieties which improve the ignition quality of the derived biodiesel, but

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the oxidative stability may compromise cold flow properties.[86] Due to the inverse relation between cold flow and oxidative stability (and cetane number), the design of an optimal fuel for all environments can be a quite difficult task. However, information obtained from simulated mixtures of oil can provide insight for the ideal fatty acid composition for fuel. Additives can play an important role, in this case, providing adjustment of the cetane number value that could not be fitted only by the composition of the diesel−biodiesel blends. A way to get oil with an increased oxidative stability and cetane number combining oleic acid and stearic acid was proposed.[87] Such fuel could be used in warmer rather than cooler climates because of the decreased cold flow associated with increased saturated fatty acid content. In addition, to combine oxidation stability (and cetane number) with enhanced lubricity, Kinney and Clemente suggested the mixture of oleic acid and ricinoleic acid, in soybean oil.[87]

Oleochemical carbonates have recently found increasing interest in commercial applications, including as biodiesel additives, due to their relatively direct synthesis in addition to their properties. Kenar et al. studied the physical and fuel properties (cetane number, low-temperature properties, kinematic viscosity, lubricity, and surface tension) of five straight-chain C_{17-39} and three branched C_{17-33} oleochemical carbonates in order to evaluate their potential as biodiesel additives.[88] These compounds showed cetane numbers ranging from 47 to 107 depending on carbon chain length and branching. For the same number of carbons, the cetane numbers of carbonate were lower than those of fatty alkyl esters with an interruption of the CH_2 chain by the carbonate moiety. The carbonates did not significantly affect cold flow or lubricity properties at concentrations up to 10 000 ppm. It was concluded that the properties of carbonates resembled those of fatty alkyl esters with similar trends resulting from compound structure and therefore were promising as cetane number additives.

On the basis of previous knowledge that compounds that enhance the octane number have a negative effect on the cetane number and vice versa, Serdari et al. studied amines of various structures as potential diesel additives, with the aim of stating the impact of the structure of these compounds on diesel and biodiesel fuel quality, mainly on cetane number and on cold-flow properties.[89] It was found that, as the chain length increased, the amine enhanced the cetane quality; in addition, methylation seemed to increase the cetane number to a larger extent than ethylation. It was concluded that the mono-dianol polyamides investigated enhanced the cetane number and also have good cold-flow performance; therefore, they may act as additives for both diesel and biodiesel fuels. The tertiary methylated fatty amines have the additional advantage of being produced from renewable starting materials (fatty acids). Tetrakis (dimethylamino) ethylene showed the best performance, but its oxidation stability must be evaluated in more detail, because of its olefinic nature.

DME also has been considered as an additive to biodiesel and diesel−biodiesel blends, due to its high cetane number. However, even small additions of DME (25%) into diesel fuel significatly reduce the viscosity of the final mixture, showing that viscosity is the limiting factor in blending DME with diesel fuel.[37]

A total of 17 additives, including commercial compounds to reduce emissions in internal combustion engines, diesel cetane improvers, and experimental/proprietary additives, were evaluated by Corporan et al.[90] Results indicated that the diesel cetane improvers and commercial smoke abatement additives tested had minimal impact on particulate emissions in the T63 turboshaft engine.

3.4. Stability Additives. Special attention is focused on the stability of biodiesel during its storage and use. Esters of unsaturated fatty acids are particularly unstable to the action of light. When exposed to air during storage, autoxidation of biodiesel can cause degradation of fuel quality by affecting properties such as kinematic viscosity, acid value, and peroxide value. One approach for increasing the resistance of fatty derivatives against autoxidation is to treat them with oxidation inhibitors (antioxidants).[91]

Mittelbach and Schober investigated the influence of different synthetic and natural antioxidants on the oxidation stability of biodiesel from rapeseed oil, sunflower oil, used frying oil, and beef tallow.[92] The four synthetic antioxidants pyrogallol (PY), propylgallate (PG), tert-butylhydroquinone (TBHQ), and butylated hydroxyanisole (BHA) produced the greatest enhancement of the induction period. The induction periods of methyl esters from rapeseed oil, used frying oil, and tallow could be improved significantly with PY, PG, and TBHQ. A good correlation was found between the improvement of oxidation stability and fatty acid composition. In 2004, the same researchers investigated the potential of different synthetic phenolic antioxidants to improve the oxidation stability of biodiesel prepared from different feedstocks.[93] At antioxidant concentrations of 1000 mg/kg, an improvement in oxidation stability could be achieved with all antioxidants tested. Variation of antioxidant concentrations between 100 and 1000 mg/kg showed that the efficiency of the antioxidants varied depending on the different types of biodiesel. Evaluation of the influence of antioxidants on critical biodiesel fuel parameters showed no negative impacts on viscosities, densities, carbon residues, CFPP, and sulfated ash contents of the different biodiesel samples. However, in terms of acid values, a noticeable increase could be observed at antioxidant levels of 1000 mg/kg. At lower antioxidant concentrations, this increase was much lower, and the values remained within the required limits.

In 2004, Miyata et al. also presented the results of oxidation stability testing on biofuels.[94] Oxidation stability was determined using three test methods, ASTM D525, EN14112, and ASTM D2274. The effects of storage condition, biofuel composition, and antioxidants on the degradation of biofuels were all studied. To further enhance stability, the addition of the antioxidants was effective, but in some cases, it also adversely affected the stability of biofuels. In the same year, a patent described the use of a liquid stock solution containing 15−60 wt % mono- or dialkyl hydroxy toluene (preferably 2,6-di-tert-butylhydroxy-

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toluene) dissolved in biodiesel fuel to stabilize it.[95] The proposed stabilized biodiesel contains 0.005−2 wt % mono- or dialkyl hydroxy toluene (preferably 0.1−1 wt %). In 2005, Dunn et al. examined the effectiveness of TBHQ, BHA, butylated hydroxytoluene (BHT), and PG in mixtures with soybean oil fatty acid methyl esters (SME). PG, BHT, and BHA were most effective. Phase equilibrium studies were also conducted to test the physical compatibility of antioxidants in SME−diesel blends. The study recommended BHA or TBHQ (loadings up to 3000 ppm) for safeguarding biodiesel from effects of autoxidation during storage. BHT is also suitable at relatively low loadings (210 ppm after blending). PG showed some compatibility problems, and it may not be readily solubilized in blends with larger SME ratios.

4. Additives for Diesel−Ethanol Blends (E-Diesel)

The number of publications and patents about E-diesel could testify to the interest in this issue in the past few years. Access of the Web of Science and Derwent Innovations Index Databases in August of 2006, taking the latest 5 years as a timespan, using <diesel and ethanol> as keywords showed that 194 documents matched the query of the 9 926 488 instances in the databases selected. For Web of Science, 108 documents matched the query of the 6 109 133 instances in the database; at the Derwent Innovations Index, 86 documents matched the query of the 3 817 355 instances.

The use of diesel−ethanol blends has been a subject of research since the first investigations were carried out in South Africa in the late 1970s.[36] E-diesel can, in principle, provide an alternative energy source by displacing diesel, a fossil fuel. More recently, since the late 1990s, it has been used on heavy-duty and light-duty diesel engines in order to modify their emission characteristics. For example, the E-diesel blends with 10% and 15% ethanol could reduce PM emissions by 20−27% and 30−41%, respectively.[22] The presence of diesel−ethanol blends generates different physicochemical properties on diesel fuel, such as reducing the density, cetane number, viscosity, lubricity, heat content, and flash point.[21,36] Material compatibility and corrosiveness are also important factors that need to be considered. Properties that affect safety should be foremost in any fuel evaluation. These include flashpoint and inflammability. Finally, fuel biodegradability has become a significant factor with respect to groundwater contamination.[36]

Ethanol used with additives such as a cetane number improver can sharply reduce particulates. The amount of improvement varies from engine to engine and also within the working range of the engine itself. However, E-diesel blends increase unburned hydrocarbons, NOx emissions, and aldehyde emissions. Moreover, the viscosity and lubricity of the blends decreases, and the cetane number linearly reduces at ambient temperature. Therefore, ignition improvers and other additives are required to improve the durability and ignition of diesel engines when E-diesel fuels are used. The potential of ethanol to reduce particulate emissions increases the flexibility to control NOx emissions at different engine operating conditions. Higher THC emissions might offer a reductant that regenerates NOx adsorbers. Other environmental benefits associated with E-diesel fuel include the improvement of biodegradability and a reduction in net emissions of greenhouse gases if ethanol is produced from biomass.

Whereas the use of ethanol in gasoline is widely practiced as a means to reduce vehicle exhaust emissions, similar use of E-diesel is not widely spread. Barriers to the use of E-diesel include limited miscibility at lower temperatures and a need for minor variations in fuel delivery systems to account for the different physical properties of ethanol as compared to diesel. An understanding of the phase behavior is necessary to achieve benefits and avoid problems when ethanol is used in diesel. Studies have been developed to find additives to keep the E-diesel blends homogeneous and stable and prevent E-diesel fuels from separating.[2]

A study reported by Li et al. indicated that the brake-specific fuel consumption and brake thermal efficiency increased with an increase of ethanol contents in the blended fuel at overall operating conditions; smoke emissions decreased especially with 10 vol % and 15 vol % of ethanol in diesel. CO and NOx emissions were reduced for E-diesel blends, but THC increased significantly when compared to neat diesel fuel.[96] Bilgin et al. aimed to determine the optimum percentage of E-diesel and the compression ratio of the engine that give the best performance and efficiency at the same time.[97] The engine was operated with E-diesel fuel having 2, 4, and 6% ethanol on a volume basis as well as with diesel fuel alone. The experiments were performed for compression ratios of 19, 21, and 23. Experimental results indicated that the addition of 4% ethanol to diesel fuel increased the power output and efficiency of the engine while it decreased specific fuel consumption for various compression ratios. The best efficiency was attained at a compression ratio of 21 with an increment ratio over 3.5%.

Experiments were performed using 5, 10, 15 and 20% E-diesel by Ajav et al.[98] Results indicated no significant power reduction in the engine operation on E-diesel blends (up to 20%) at a 5% level of significance. Brake-specific fuel consumption increased by up to 9% with an increase of ethanol up to 20% in the blends as compared to diesel alone. The exhaust gas temperature, lubricating oil temperatures, and exhaust emissions (CO and NOx) were lower with operations using E-diesel blends as compared to operations using undiluted diesel.

Smoke emission can be remarkably reduced with E-diesel. The improvement of smoke emission can be explained by enrichment of the oxygen owing to ethanol.[23] Considering the results of smoke emission, which is closely related to particulate matter emission, adding ethanol to biodiesel and diesel fuel blends results in a significant improvement in particulate matter emissions.[22]

Adam et al. considered that ethanol and methyl-tert-butyl ether (MTBE), although beneficial in reducing atmospheric pollution, may increase groundwater contamination due to the cosolvency of petroleum hydrocarbons and by the provision of a preferential substrate for microbial utilization.[99] The levels of ethanol addition investigated were at the current additive level (approximately 25%) for ethanol additive fuels in Brazil and values above (50%) and below (10%) this level. The authors concluded that sand grains might have a more important role in the adsorption of petroleum hydrocarbons than first realized. Despite the fact that the fuel additive MTBE had been used in an effort to improve air quality, other undesirable effects, particularly the contamination of water resources, have eventually been judged to overcome any air quality benefits it might

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have offered. The experience with MTBE illustrates the need to evaluate potential positive and negative environmental impacts associated with fuel choices using a comprehensive approach, referred to as "comprehensive environmental assessment" (CEA), that combines a product life-cycle perspective with the risk assessment paradigm.[100]

The most important advantage of E-diesel is that it can be used without any modification in diesel engines.[36] Studies have shown some promise of solving the chronic problems with blends of 10−40 vol % ethanol in diesel fuel. One of the primary problems is that ethanol has a low cetane number. Modern diesel engines need a cetane number of 40 or higher to give their intended performance and emissions. This problem can be solved with cetane-enhancing additives, such as 2-ethylhexyl nitrate.[77] The lubricity of the fuel is another concern. The diesel fuel injection system relies on the fuel for the lubrication of its closely fitting parts. Ethanol has poor lubricity, so it degrades the lubricity of the diesel fuel. However, this problem can also be solved with a lubricity additive. Finally, the flashpoint of E-diesel is a problem, and it cannot be corrected with an additive. The flashpoint of a fuel is the temperature where the vapors above the liquid fuel can be ignited. Ordinarily, diesel fuel has a flashpoint that is around 52−65 °C. This means that there is little chance of accidentally igniting diesel fuel, and it is sometimes called an "intrinsically safe" fuel. However, with ethanol presence, the flashpoint will be below ambient temperatures, and the fuel needs to be treated with the same precautions as gasoline.

It was found that, due to technical limitations, ethanol does not blend effectively with diesel to form stable solutions. E-diesel blends are not accurately described as either miscible or immiscible. Solubility of ethanol in diesel depends on the hydrocarbon composition and wax content of the base diesel, ethanol content (a low ethanol concentration has reduced immiscibility), and the temperature of the diesel fuel.[96] Lowering the diesel aromatic content reduces the solubility of ethanol.[101]

One of the main parameters of E-diesel is stability at low temperatures. Anhydrous ethanol easily blends with diesel to form stable solutions containing up to 5% ethanol at warm ambient temperature.[77] However, at temperatures below 10 °C, ethanol is immiscible in diesel, and the blend separates into two phases. This fact affects the fluidity and good filterability of the E-diesel in cold climatic conditions.[36]

Solubility also depends on the water content of ethanol. Ethanol is hygroscopic and easily picks water up from ambient air and from the distribution system. Anhydrous ethanol is highly soluble in diesel fuel at contents of approximately 0−30% and 70−100%. Within these zones, the miscibility and the cloudiness in the mixture followed by phase separation have been observed when the water content of the ethanol exceeded 1%.[21] Therefore, low temperatures and/or water contamination result in fuel instability due to phase separation. To stabilize the blend in the presence of a high water content and to ensure fuel homogeneity under all conditions of the temperature, additives are indispensable in E-diesel.[21,96] However, these additives increase the fuel's cost.[36]

There are two additive-based approaches to maintaining stable blends: adding surfactants (emulsifiers) that produce stable emulsions or microemulsions or adding cosolvents that produce stable solutions. Cosolvents act as a bridging agent through molecular compatibility and bonding to produce a homogeneous blend. Cosolvents can be prepared by splash blending, which is just pouring the components together into a tank (storage tank or tank truck). Preparing an E-diesel blend with surfactants is more complicated. Normally, this preparation requires a heating and stirring step.

A microemulsion consists of droplets or micelles of ethanol dispersed in the diesel fuel phase, and a small amount of emulsifier and water is required for its formation. E-diesel formulations are most likely microemulsions. A work from the 1980s focused on emulsifiers, and the first E-diesel microemulsion was described by Moses et al.[102] In their study, about 2% of a commercial surfactant was required for each 5% of aqueous ethanol (5% water) added to diesel fuel to form a spontaneous, transparent, and thermodynamically stable blend. Boruff et al., in 1982,[103] used a mixture of two surfactants, N,N-dimethylethanoamine and unsaturated fatty acids, at a concentration in excess of 10 vol %, with aqueous ethanol and diesel. They report that blends were stable at temperatures as low as −15.50 °C. Since that time, emulsifier technology has advanced, and today less than 1 vol % is required in some cases. Makareviciene et al. studied the solubility of fatty acid ethyl ester (rapeseed oil ethyl ester) and fatty acid methyl ester (rapeseed oil methyl ester) in E-diesel blends and reported that the blends were formed instantaneously in a wide range of component concentrations.[104] Fernando and Hanna attempted to use biodiesel as a potential amphiphile in the E-biodiesel system.[105] They studied the phase behavior of the ethanol−biodiesel−diesel ternary system in order to identify key areas within the phase diagram that are stable isotropic microemulsions that could be used as potential biofuels for compression-ignition engines. The instantaneous phase behavior indicated that the system formulates stable microemulsions over a fairly large region of the phase triangle, depending on the concentrations of different components. The single-phase area of the three-component system was widest at higher biodiesel concentrations. The phase diagram indicated that, at higher diesel concentrations, in order to formulate a stable microemulsion, the ratio of biodiesel to ethanol in the system should be greater than 1:1. The results of the study suggested that biodiesel could be effectively used as an amphiphile in an E-diesel blend.

Satgé de Caro et al. selected two organic additives with different physicochemical parameters to study the behavior of an E-diesel mixture.[21] These compounds had a glycerol skeleton bearing heteroatoms and amino-ether, hydroxyl, nitrate, and nitramine functional groups. These nonionic surfactants act by reducing the interfacial tension in a liquid medium and homogenizing the E-diesel blend. Engine behavior seemed to be improved in the presence of additives with a reduction of pollutant emissions in exhaust gas, cyclic irregularities, and ignition delay. No trouble-shooting, knocking, or vapor-lock phenomenon was encountered during this study.

Tetrahydrofuran and ethyl acetate were identified as effective cosolvents for E-diesel blends.[36] Can et al. added 1% isopropanol to ethanol (10 vol % and 15 vol %)−diesel blends to satisfy homogeneity and prevent phase separation.[106] The

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aromatic contents will affect the amount of additive used. In low aromatic content diesel, a high amount of additive is required.

Currently, there are five predominant blend additive packages, from different suppliers, that allow the preparation of stable E-diesel blends generally containing 10−15% ethanol. Four of these additives are cosolvent-based:[36] (*i*) *Puranol*, invented by Pure Energy Corporation, was the first additive package (using a 1−5% dosage with 15% anhydrous ethanol) that creates a stable solution of ethanol in diesel. (*ii*) OxyDiesel (formely AAE Technologies of the United Kingdom) allowed the production of a blend using a 1% dosage with 7.7% ethanol. Finally, there are (*iii*) Beraid ED-10 (Akzo Nobel) and (*iv*) *Purinox* (Lubrizol Corporation), while GE Betz (formely Betz−Dearborn, a division of General Electric, Inc.) is an emulsifier derived purely from petroleum products.[107]

In Brazil, *Ecológica Mato Grosso Indústria e Comércio Ltda* prepared the additive AEP-102, from soy oil. The additive is biodegradable, acts as a cetane improver, and presents good solubility and lubricity properties. AEP-102 contributes to stabilization of the E-diesel. The mixture with 89.4% diesel, 8% ethanol, and 2.6% AEP-102 presented excellent performance.[108] Researchers had successfully tested, in urban buses, a blend of 86% diesel, 11% anhydrous alcohol, and 3% AEP-102 additive.[109]

Some others additives have been tested to solve the problems associated with E-diesel. Four different ethanol−1-butanol−diesel microemulsions were tested by Bhattacharya et al.[110] in a constant-speed, direct-injection diesel engine rated at 7.4 kW. The stable and homogeneous microemulsions were obtained by mixing 160-, 170-, and 180-proof ethanol−1-butanol−diesel in a 1:2.5:5.5 ratio as well as 180-proof ethanol−1-butanol−diesel in 1:2:3 proportions. The characteristic fuel properties such as relative density, kinematic viscosity, and gross heat of combustion of the microemulsions were found to be close to that of diesel fuel. The power-producing capability of the engine was found to be similar using diesel fuel and the microemulsions. The emission of CO was found to be marginally lower, but that of unburnt hydrocarbons and NOx were higher using microemulsions.

The effect of ether additives in diesel and of ether/ethanol/diesel blends on the properties of density, volatility, viscosity, characteristics at cold temperatures, cetane number, and performance in engine tests was evaluated by De Menezes et al.[33] The results indicate that ethyl tert-butyl ether (ETBE) and tert-amyl ethyl ether act as cosolvents of E-diesel. The presence of ethanol and ETBE significantly alter the characteristics of volatility (flashpoint and distillation curve) and reduce the cetane number, impairing the fuel's performance in engine tests.

He et al. used an additive to keep the E-diesel blends homogeneous and stable and an ignition improver, which can enhance cetane number of the blends.[2] These additives had favorable effects on the physicochemical properties related to ignition and combustion of the blends with 10% and 30% ethanol by volume. At high loads, the blends reduce smoke significantly with a small penalty on CO, acetaldehyde, and unburned ethanol emissions compared to diesel fuel. NOx and CO_2 emissions of the blends are decreased somewhat. At low loads, the blends have slight effects on smoke reduction due to an overall leaner mixture. With the aid of additives and an ignition improver, CO, unburned ethanol, and acetaldehyde emissions of the blends can be decreased moderately; even total hydrocarbon emissions are less than those of diesel fuel. The results indicate the potential of diesel reformation for clean combustion in diesel engines.

Volatile organic compounds (VOCs) play a significative role in the formation of photochemical smog. Photooxidants are formed in the atmosphere when VOCs react with NOx, in the presence of sunlight and $OH^{\bullet}$ radicals. In urban areas, vehicle fuels constitute an important source of VOC and NOx emissions to the atmosphere, either by burning or by evaporative losses.[111−114] A comparative study of the two types of light-duty vehicular fuels presently used in Brazil—gasohol and hydrated ethanol—as potential precursors for ozone formation in the atmosphere of urban cities was conducted outdoors, using two Teflon chambers which were filled, respectively, with each fuel, at high initial VOC-to-NO ratios and exposed to the sunlight. Ozone formation as well as NOx concentration profiles were measured directly using ozone and NO/NO_2/NOx continuous analyzers. The results showed that, for the same initial volumes of the two fuels in the bags, the ozone peak concentrations are on average 28% higher for alcohol compared with gasohol. In addition, the ozone formation process showed a tendency to start earlier for gasohol, but once started, its concentration increased 2 times faster for the alcohol fuel.[115]

5. Perspectives

Two basic trends are driving the up-to-date research and marketing of diesel additives: the progressive reduction of sulfur content and the increasing use of biofuels. The first should be applied not only to diesel but also to their blends (E-diesel, biodiesel−diesel, biodiesel−ethanol−diesel, and vegetable oil mixes). The additives for biofuels must observe emission regulations and motor and combustion requirements, and their composition and concentration are highly dependent on the biodiesel source.

The recent introduction of ultralow-sulfur diesel (ULSD or S15) with less than 15 ppm, for example, 97% of the 500 ppm current on-road diesel, is specified by ASTM D975 in North America and EN540 in Europe and aims to reduce NOx and particle emissions as well as enable latest-technology high-

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pressure common rail and other fuel-injection equipment (FIE) systems to operate properly. Although, it is more expensive, has a lower lubricity and a lower energy content (MGP), and might be prone to seal leaks and wear-related problems.

These regulations also apply to any diesel fuel products, which must be clearly labeled if they meet or do not meet the ULSD specifications. Additives will also need to comply with these requirements.

The growing popularity of biodiesel blends is closely related with emissions legislation and the increasing desire for renewable energies, although their economic viability will depend on international crude oil prices and on the market price of biodiesel coproducts.

Although biodiesel is renewable and has good lubricity, it has several drawbacks that will need to be addressed: it is more expensive than diesel, has a lower energy content, has water contamination, does not have good operation under cold weather, is corrosive, often contains methanol, has short shelf life, and affects fuel filters.

Most of the biodiesel specifications are unregulated as yet, resting on a big concern regarding recycled oils. Nevertheless, most engine original equipment manufacturers approve B2 or B5, and all major FIE manufacturers approve B5; some (Cummins, Case, and New Holland) approve B20 in certain engines. The identification of efficient additives should boost their regulation. Although there is no formal specification for blended biodiesel, it is expected to meet ASTM D975 standards (which means bio and ULSD blends).

Biodiesel has also a huge cross-section of consumers with very different levels of knowledge and needs: environmentalists, the “budget conscious”, farmers, and state or city authorities. It will probably bring more problems, and there are not as many solutions; thus, new additive formulations will be needed to work for different problems. The most pressing are those preventing cold weather problems—needing a heater, quicker degradation/oxidation, corrosion of metal parts, rubber seals leakage, and filters choking quicker. Cold additives are needed for improving the cold-flow properties of biodiesel for applications as a neat fuel and in blends with petro-diesel, improving the cloud point, pour point, cold filter plugging point, and low-temperature flow.

Depending on the biodiesel source, its specifications and, consequently, the additive requirements will vary. The most known sources of oils/fats are usually SME, rapeseed (canola) methyl ester, palm methyl ester, and yellow greases (e.g., waste cooking oil). They yielded the range of possible specifications that allowed the institution of ASTM 6751 (North America) or EN14214 (Europe), to which biodiesel should comply. In recent years, several new biodiesel sources have been reported: rapeseed oil, palm kernel oil, rice bran oil, corn oil, castor bean oil, jatropha curcas, sun flower oil, and plant sludges. Each of these biodiesels will need to be studied with known and new additives.

Specially recycled fast food oil and homemade fuel will especially need additives to avoid lots of repair work.

To make biodiesel economically viable, it is also necessary to propose new uses for its coproducts, one of them as an additive. In the process of biodiesel production through basic catalysis, glycerol is obtained as a coproduct in an amount equal to 10% of the esters by weight. Thus, in the interest of maintaining international glycerol value, a combination of biodiesel and glycerol ethers has been suggested by Spooner-Wyman et al. as an additive to diesel fuel.[116] The study used a screening methodology to evaluate some glycerol derivatives. The total PM, total volatile fraction, NOx, CO, THC, CO_2, and O_2 were measured for several blends and a base fuel. On the basis of total PM emissions and other considerations, the study concludes that di-butoxy glycerol is a promising candidate for blending in diesel fuel. There are studies that mention diesel fuel additives containing glycerol acetals and glycerol acetal carbonates.[113,114]

Last but not least relevant is the definition of worldwide regulations. It is likely that compliance to North American and European regulations by other regions of the planet will not be straightforward due to the specificities of the local sources of biodiesel and of the weather conditions. This item is quite relevant for worldwide energy trade barriers that might become forbidden. If this issue is not clear in reasonable time, the diplomatic and world trade organizations might find themselves facing issues that are quite hard to overcome. Here, worldwide approval of additives might become an indispensable tool.

It is necessary to highlight the worrisome lack of available toxicity studies and information regarding how the new additives and fuels modify the toxicity of the engine exhaust emissions, both in terms of PICs and the unburned additives themselves, as well as secondary toxic species formed during atmospheric transport. This kind of information is indispensable to evaluate potential positive and/or negative environmental impacts associated with additives and fuel choices, avoiding a situation that decisions be made on the basis of mainly economic considerations.

6. Conclusions

Due to the worldwide effort to make renewable energy economically viable as well as to use cleaner fuels, additives will become an indispensable tool in global trade. Their technical specifications not only cover a wide range of subjects but also most subjects are interdependent. This makes the expertise of additives technology indispensable in the global trade of fuels. It is likely that, as energy sources become cleaner and renewable, we might find ourselves facing issues that are quite hard to overcome, and diesel additives may become a worldwide indispensable tool. The additives share in the world market should increase in the next few years as long as energy sources become cleaner and renewable.

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