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Effect of Nano-catalysts on the Combustion Performance of Bio-ethanol

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Abstract: Currently, there is a strong need to develop new engines that incorporate advanced propulsion technologies. However, these systems place severe demands on combustion and thus methods to improve combustion by reducing ignition delay or widening the stable flame conditions are also required. Although a catalyst would allow combustion to begin at lower temperatures, it is not practical to install a catalyst in an engine combustor. Therefore, new methods for contacting the catalyst with the fuel/air mixture are required. Investigations of improving ignition and combustion characteristics with different methods have proliferated in the literatures. For example, engine optimization, ignition enhancer, and heterogeneous catalyst. A feasible way is to dissolve the catalyst in the fuel so that it can be added continuously. To be effective, the catalyst must meet several criteria: (1) it must have good activity for hydrocarbon combustion; (2) it must be well dispersed in hydrocarbon fuels at nanometer scale. Results demonstrate that a soluble nano-catalyst has the potential to significantly reduce the ignition delay and also to widen the range of stable flame conditions.

Keywords: Nano-catalysts, Bio-ethanol, Combustion.

مطالعه اثر نانوکاتالیست بر عملکرد احتراق بیواتانول

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چکیده: اخیراً، بمنظور استفاده از فناوری‌های پیشرفته نیروی محرکه، نیاز مبرمی به توسعه موتورهای جدید می‌باشد. بهرحال این سیستم‌ها برمبنای احتراق کار می‌کنند و بنابراین روش‌هائی موردنیاز است که بتوان بوسیله کاهش تاخیر در جرقه و یا گسترش شرایط شعله چایدار، عملکرد احتراق را بالا برد. گرچه یک کاتالیست می‌تواند موجب بروز احتراق در دمای پائین شود ولی از نظر فنی نمی‌توان کاتالیست را در محفظه احتراق نصب نمود. بنابراین روش‌های جدیدی را برای تماس کاتالیست با مخلوط سوخت و هوا موردنیاز است. پیشینه تحقیق شامل تحقیقات زیادی در زمینه اصلاح جرقه و مشخصه‌های احتراق می‌باشد. بعنوان مسثال، بهینه‌سازی موتور، ارتقادهنده جرقه و کاتالیست یکنواخت. یک راه عملی عبارت از حل کاتالیست در سوخت بطوریکه آن بطور پیوسته اضافه شود. برای تأثیر بیشتر کاتالیست باید دارای چندین معیار باشد از قبیل فعالیت خوب برای احتراق هیدروکربور و اختلاط خوب با سوخت‌های هیدروکربور در مقیاس نانومتر. نتایج نشان می‌دهد که کاتالیست نانو و قابل حلدر سوخت دارای قابلیت بیشتر جهت کاهش قابل ملاحظه تأخیر در احتراق بوده و همچنین می‌تواند شرایط شعله پایدار را در محفظه احتراق گسترش دهد.

واژه های کلیدی: نانوکاتالیست، نانواتانول و احتراق.

1. Introduction

As the fossil fuels reserves are reducing at a faster rate as result of the population growth and the ensuing energy utilization, in recent years an urgent need to find renewable alternative fuels has emerged. The danger of global warming and the stringent government regulations have attracted the engine manufacturers and the consumers in improving combustion rate of fuels and following safer emission norms to save the environment from pollutions and also save fossil fuels for coming population. These limitations have led researchers towards finding alternative sources of energy. Among the various renewable fuels, bioethanol has the ability to generate vast amounts of energy in an environmentally-friendly way. This source of energy is noticed as the most desirable fuel extenders because each owns unique advantageous properties: 1) it is renewable in nature [1] 2) it is capable of powering a car or other large machines while the byproduct is only water [2] and 3) because of its high oxygen content, its combustion being complete [3]. In a combustion process, hydrocarbons present in a common fuel are ignited to create energy, water and carbon dioxide. However, impurities in fuels coupled with inefficient reactions yield harmful byproducts such as carbon monoxide, nitrogen dioxide, and sulfur hexafluoride [4,5,6]. These compounds can lead to ozone depletion, acid rain, and other environmental worries. Among the various techniques available to improve combustion, reduce ignition delay, and reduce the harmful byproducts from exhaust emissions, applying fuel-borne catalysts is preferred. In other words, fuel-borne catalysts increase fuel efficiency by reducing harmful greenhouse gas emissions and the health-threatening chemicals such as NO_x, CO_2, CO, etc. and particulate matters according to completion of combustion [7,8]. Therefore, catalytic combustion of fuels is a promising technology for producing energy, since it leads to very low emissions of unburned hydrocarbons [9]. Up to this date, many studies have been carried out on the application of catalysts to improve combustion of several fuels such as rocket fuels (for their significance in military programs) [10,11] and other hydrocarbon fuels [12,13,14,15,16, 17]. For example, using catalysts to improve the combustion of methane as the main component of natural gas has been of particular interest. This is due to unique features of Methane: 1) its large ready-to-use world reserves and 2) it generally contains low amounts of sulfur and nitrogen containing compounds [12].

Conventionally, the promotion of the oxidation reaction, which is the most important reaction in combustion, is accomplished through the use of expensive Platinum catalysts [2]. Heterogeneous catalysts such as Nickle [18] have also been used vastly to boost the combustion behavior of different fuels. Despite of their attractive advantages, there are a few drawbacks associated with their application including deactivation at high temperatures and settling out during reaction [8]. Hence, for promoting catalytic fuels combustion, it is therefore, necessary to develop catalysts with high-catalytic activity, stability at high temperatures and non-perceptible during injection and combustion process. Nano-catalysts not only have the potential to make fuel combustion complete and fast, decrease ignition time, and therefore produce little or non-toxic byproducts but also do not hold the above-mentioned shortcomings [7]. The large surface areas of nano-scale catalysts as well as reports on novel chemical reactivity of particles with nanometer dimensions make these materials highly interesting [14].

The aim of this review is to highlight the importance of fuel-born nano-catalysts in improving combustion behaviors of bio-ethanol and its consequent role in economizing and promoting bio-fuels worldwide.

2. Bio-ethanol

By 2020, the world consumption of oil and oil products will increase by 20–50% according to various estimates. The limited quantity of fossil fuels on the planet has led researchers towards finding alternative sources of energy which have the ability to generate vast amounts of energy in an environmentally friendly way. Many countries and international organizations have set challenging targets for the partial replacement of conventional fossil fuel sources with renewable bio-fuels to combat energy shortages and climate change [19]. Transportation and agricultural sector is one of the major consumers of fossil fuels and biggest contributor to environmental pollution, which can be reduced by replacing mineral-based fuels by bio-origin renewable fuels. Two major conditions for development of renewable fuels manufacture technologies in the world are exhaustion of oil resources and tightening environmental standards for motor fuels. It is expected that production of synthetic liquid fuels (SLF) will become a sector of the international oil and gas industry in the nearest future [4]. SLF–diesel fuel can be applied with success as "an environmental additive." In other words, more pure SLF–diesel fuel can be mixed with usual diesel fuel with the purpose to increase qualitative characteristics of the latter. A broad feedstock base is an important feature of production of synthetic liquid fuels. Such fuels can be produced practically from any carbon-containing feedstock, such as coal, natural gas, biomass of various origins, etc.

The following substances are considered now as promising synthetic fuels [4]:

- Synthetic liquid fuels, analogs of respective oil products (gasoline, kerosene, diesel oil)
- Bio-ethanol
- Di-methyl ether
- liquefied petroleum gas (a mixture C3–C4 hydrocarbons, a product of oil extracting or oil refining)
- Liquefied natural gas
- Ethers of vegetable oils produced from fruits or seeds ("biodiesel fuel" or "biodiesel" is one such clean bio-fuel that can be readily synthesized via transesterification of natural animal fats or vegetable oils with C1–C2 alcohols.
- Bio-ethanol: Bio-ethanol produced by fermentation of biomass of various origins such as corn or sugar cane.
- Hydrogen

Among the above fuels there are two global liquid transportation bio-fuels that might replace gasoline and diesel fuel; these are bio-ethanol and bio-diesel [19]. Bio-ethanol is used as a gasoline replace-ment and is a petrol additive/substitute that can be produced from plentiful, domestic, cellulosic biomass resources such as herbaceous and woody plants, agricultural and forestry residues, and a large portion of municipal and industrial solid waste streams. Production of bio-ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution. In 2004, 3.4 billion gallons of fuel bio-ethanol were produced from over 10% of the corn crop. Bio-ethanol demand is expected to more than double in the next 10 years. For the supply to be available to meet this demand, new technologies must be moved from the laboratories to commercial reality [19]. The world bio-ethanol production is about 60% from feedstock from sugar crops. The feed stocks used for bio-ethanol production are cereals and sugar beet bio-ethanol production used 0.4% of EU cereals production and 0.8% of EU sugar beet production. Brazil was the world's leading bio-ethanol producer until 2005 when US production roughly equaled Brazil's. The United States became the world's leading bio-ethanol producer in 2006. The People's Republic of China holds a distant but important third place in world rankings, followed by India, France, Germany and Spain. figure 1 shows the top five bio-ethanol producers in 2006.

Bio-ethanol can be used directly in cars designed to run on pure bio-ethanol or blended with gasoline to make ''gasohol". Anhydrous bio-ethanol is required for blending with gasoline. No engine modification is typically needed to use the blend. Bio-ethanol can be used as an octane-boosting, pollution-reducing additive in unleaded gasoline. World production of bio-ethanol from sugar cane, maize and sugar beet increased from less than 20 billion liters in 2000 to over 40 billion liters in 2005. This represents around 3% of global gasoline use. Production is forecasted to almost double again by 2010 [4,19]. Alcohols have been used as a fuel for engines since the 19th century. Among the various alcohols, bio-ethanol is known as the most suited renewable, bio-based and eco-friendly fuel for spark-ignition (SI) engines. The most attractive property of bio-ethanol as an SI engine fuel is that it can be produced from renewable energy sources such as sugar, cane, cassava, many types of waste biomass materials, corn and barley. In addition, bio-ethanol has higher evaporation heat, octane number and flammability temperature therefore it has positive influence on engine performance and reduces exhaust emissions. The results of the engine test showed that bio-ethanol addition to unleaded gasoline increase the engine torque, power and fuel consumption and reduce carbon monoxide (CO) and hydrocarbon (HC) emissions [12]. An experimental investigation was conducted to evaluate the effects of using blends of bio-ethanol with conventional diesel fuel, with 5% and 10% (by vol.) The results of the statistical analysis suggest that the use of E10 results in statistically significant decreases in harmful emissions.

The biggest difference between bio-fuels and petroleum feed stocks is oxygen content[3]. Bio-fuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of bio-fuels very different from petroleum. Oxygenates are just pre used hydrocarbons having structure that provides a reasonable antiknock value. Also, as they contain oxygen, fuel combustion is more efficient, reducing hydrocarbons in exhaust gases. The only disadvantage is that oxygenated fuel has less energy content. The combustion is the chemical reaction of a particular substance with oxygen.

Combustion represents a chemical reaction, during which from certain matters other simple matters are produced, this is a combination of inflammable matter with oxygen of the air accompanied by heat release. The combustion process is started by heating the fuel above its ignition temperature in the presence of oxygen or air. Under the influence of heat, the chemical bonds of the fuel are cleaved. If complete combustion occurs, the combustible elements (C, H and S) react with the oxygen content of the air to form CO_2, H_2O and mainly SO_2. If not enough oxygen is present or the fuel and air mixture is insufficient then the burning gases are partially cooled below the ignition temperature and the combustion process stays incomplete. The flue gases then still contain combustible components, mainly carbon monoxide (CO), unburned carbon (C) and various hydrocarbons (C_xH_y).

Bio-ethanol has a higher octane number (108) [4,19], broader flammability limits, higher flame speeds and higher heats of vaporization than gasoline. These properties allow for a higher compression ratio, shorter burn time and leaner burn engine, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine. The octane number of bio-ethanol allows it to sustain significantly higher internal pressures than gasoline, before being subjected to pre-detonation.

3. Nanocatalysts

One of the thriving areas of research in chemistry is the search for ways to speed up reactions without increasing temperature (which is expensive). As we know when examining the Arrhenius equation:

$$K=A\exp(-Ea/RT)$$

One important factor in the rate of reaction is the activation energy. The larger Ea, leading to smaller k and slower reaction. Lowering the Ea with catalysts is one approach. A catalyst provides an alternative reaction pathway, which has lower activation energy [5]. On the other hand a catalyst is a material that increases the speed of a reaction in one of three ways [6]; it can lower the activation energy for the reaction through a change of reaction mechanism, act as a facilitator and bring the reactive species together more effectively, or create a higher yield of one species when two or more products are formed. Catalysts do not show up in the overall chemical reaction (they are typically conserved to react over and over).

One class of catalysts are homogeneous catalysts which react in the same phase as the chemical reaction of interest. For example, a homogeneous catalyst is a liquid catalyst in a solution, gas catalyst in the gas phase. To be effective, the homogeneous catalyst must meet several criteria [8]. First, it must have good activity for reaction so that very little catalyst is required. Second, it must be finely divided (at the nanometer scale) so that it can be accessible to as much of the reactant as possible. Finally, it must be soluble in the reactants, both to disperse it and simply to keep it from settling out during reaction. Nano-materials are more effective than conventional catalysts for two reasons [7,8]. First, their extremely small size (typically 10-100 nanometers) yields a tremendous surface area-to-volume ratio. Also, when materials are fabricated on the nano-scale, they achieve p-roperties not found within their macroscopic counterparts. A key concept to understanding nano-catalysis involves the ratio of surface area and volume. As an object gets larger, its surface area increases less in relation to its volume [2,8,9]. For comparison, the length scale of a hydrogen atom is the order of 0.1 nm. A spherical particle having a diameter of a few nanometers contains only thousands of atoms. Therefore, the ratio of surface atoms to bulk atoms increases dramatically as the diameter of the particle decreases. Because surface atoms have a lower coordination, the electrical and thermo-physical properties are vastly different than the bulk atoms. When the surface to bulk atom ratio becomes significant, the bulk material can begin to exhibit the properties of the surface atoms.

4. Use of catalysts in fuels

In fuels the reduction in activation energy allows the combustion reaction and accompanying heat release to begin at a lower temperature than would otherwise be possible, effectively reducing the auto ignition time [14]. Also The increased kinetics of the reaction releases heat more quickly, and therefore makes the reaction more intense improving fuel efficiency can have drastic effects: both environmentally and economically [15]. Improving the rates of catalytic combustion occurs through product selectivity.

In a common automobile, hydrocarbons in the gasoline ignite to create water, carbon dioxide, and the force necessary to drive the engine's pistons. However, impurities in gasoline coupled with inefficient reactions yield harmful byproducts such as carbon monoxide, nitrogen dioxide, and sulfur hexafluoride [16]. These compounds can lead to ozone depletion, acid rain, and other environmental concerns [17].

Auto ignition times in hydrocarbon fuels have traditionally been of interest in both gasoline and diesel engines, and most research has been done in the temperature and pressure ranges characteristic of these applications [18]. Historically, peroxides and alkyl nitrates have been found to be the most effective in promoting auto ignition [7]. Recent work suggests that alkyl nitrates are still the compounds of choice for reducing ignition delays in diesel fuels, with 2-ethyl-hexyl nitrate (2-EHN) being the current favorite [8]. The $RO–NO_2$ bonds in alkyl nitrates are relatively weak and therefore they break easily, producing molecular fragments that contain an unpaired electron, or a free radical. The presence of the free radicals allows the combustion process to occur at lower temperatures, thereby improving the Cetane number (a measure of a fuel's ignition delay). Although progress has been made with ignition enhancers, these compounds only produce small increases in the rates of existing reactions in the combustion process. A substantially different approach, which has the potential to produce major improvements in combustion, is the use of heterogeneous (or solid) catalysts that they are in a different phase than the overall reaction. But there are a few drawbacks associated with their application including deactivation at high temperatures and settling out during reaction [8].

5. Use of Nano-catalysts in fuels

Unfortunately, the use of a traditional, solid catalyst would not be practical because continuously exposing a supported catalyst to the extremely high temperatures encountered in a combustion environment would quickly deactivate the catalyst. Therefore, other methods to contact the catalyst with the fuel/air mixture are needed. One way to introduce the catalyst would be to dissolve it in the fuel so that it is added on a continuous basis. Recently, a proprietary technology developed, which refer to as alumoxane chemistry, to produce alumina-based compounds that have a wide range of attractive properties [8,12]. Carboxylato-alumoxanes (Fig. 2) are very small boehmite particles (Fig. 3) covalently bound to several carboxylic acids groups and have several characteristics that make them potentially useful as combustion catalysts [8]. First, the boehmite particles are very small, between 20 and 200 nm, and therefore they can be dispersed very effectively in the combustion zone. In addition, the functional group on the carboxylic acid R can be adjusted to make the particles soluble in a wide variety of liquids.

An experimental investigation is carried out to establish the performance and emission characteristics of a compression ignition engine while using cerium oxide nano-particles as additive in neat diesel and diesel-biodiesel-bio-ethanol blends [7]. Performance characteristics are studied using the stable fuel blends in a single cylinder four stroke computerized variable compression ratio engine coupled with an eddy current dynamometer and a data acquisition system. The cerium oxide acts as an oxygen donating catalyst and provides oxygen for the oxidation of CO or absorbs oxygen for the reduction of NO_x. The activation energy of cerium oxide acts to burn off carbon deposits within the engine cylinder at the wall temperature and prevents the deposition of non-polar compounds on the cylinder wall results reduction in HC emissions. The tests revealed that cerium oxide nano-particles can be used as additive in diesel and diesel-biodiesel-bio-ethanol blend to improve complete combustion of the fuel and reduce the exhaust emissions significantly.

6. Outlook and future

Indiscriminate extraction and lavish consumption of fossil fuels have led to reduction in underground-based carbon resources, so it is necessary to look for alternative fuels which can be produced from resources such as alcohol, biodiesel, vegetable oils etc. Bio-fuels are promising renewable energy sources, a harmonious correlation with sustainable development, energy conservation, efficiency and environmental preservation. There are a variety of bio-fuels potentially available, but the main bio-fuels being considered globally are biodiesel and bio-ethanol. Bio-ethanol can be blended in any proportion with mineral diesel to create a blend. The use of bio-ethanol in conventional engines results in substantial reduction in emission of unburned hydrocarbons, carbon monoxide and particulate. There are several studies on bio-fuels properties, their application, combustion, etc; but no study on the application of nano-catalysts on the bio-fuels combustion performance is reported. According to effect of these catalysts on improving combustion efficiency of petroleum fuels and also the future of bio-fuels, it seems to be fine, study and research on this field; especially use of soluble nano-catalysts is more preferable because of their specific properties as discussed in this paper. While the combustion and energetic materials communities have lagged in the usage of nanotechnology, it is clear that soon many areas of combustion will be influenced by nanotechnology as a result of future fuels.

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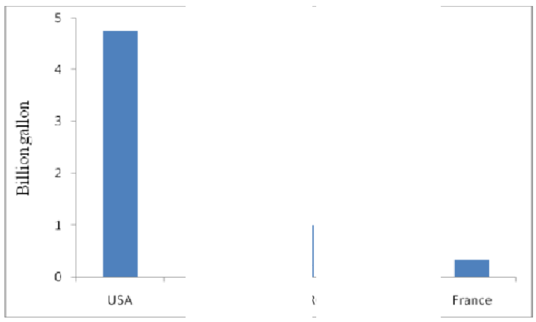

Fig. (1): The top bio-ethanol producers in 2006.

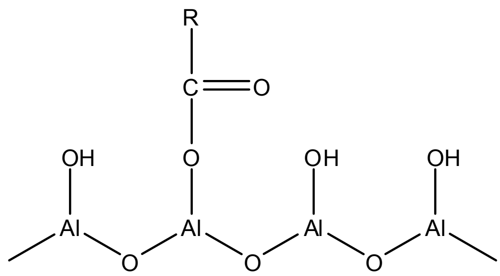

Fig. (2): Molecular structure of Carboxylato-alumoxane

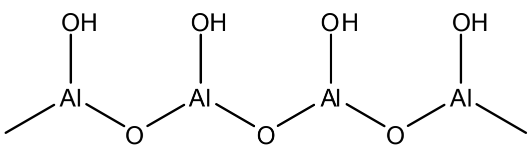

Fig. (3): Molecular structure of Boehmite nano-particles