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Carbonyl and aromatic hydrocarbon emissions from diesel engine exhaust using different feedstock: A review

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ABSTRACT

The depleting natural resources, primarily petroleum that has been the backbone of fuel industry is finding itself at loss to answer the questions of our future needs. This has led researchers to venture into the area of biodiesel since it is the next best contender to replace diesel in the immediate future. This is so because biodiesel has characteristics not only similar to diesel but also better in many respects, like biodegradability, renewability and better emission characteristics. Many authors have studied regulated emission characteristics. The results are in favour of biodiesels in terms of carbon monoxide, smoke, hydrocarbons (*HC*) and particulate matter (*PM*). The study in the area of unregulated emissions is, however, limited and inconsistent, even though they are considered carcinogenic and mutagenic in nature. Hence, for a better understanding of biodiesel and their emissions, it is necessary to examine their unregulated emissions as well. This paper consolidates and analyses data regarding carbonyl, polyaromatic hydrocarbons (*PAHs*) and their oxy and nitro derivatives of various biodiesels derived from various feedstock and their diesel and alcohol blends. The emission trends have also been studied for various parameters like engine speed, engine load, driving cycle etc.

Contents

1. Introduction

Due to hike in oil prices, increasing demand of energy, limited availability of resources for fossil fuels, impact on environment etc. forced the researchers towards a fuel, which have the capability of fulfilment global energy demand as well as characteristics like technical feasibility, domestic availability and environmental acceptability. The main consumer of energy is transport sector and primarily based on diesel. The cost of diesel fuel increases as demand increases which becomes a great setback to economy. To overcome these problems from fossil fuels, it is necessary to find out the alternative fuel. Therefore, the researchers focussed on the straight vegetable oil and its derivatives like biodiesel. Biodiesel is found to be the most important alternative fuel used in conventional diesel engines, as its characteristics are similar to

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Nomenclature

ACE	Acetaldehyde
AcP	Acenaphthene
AcPy	Acenaphthylene
ACR	Acrolein
AM	Artemis motorway
AN	Animal fat
AnT	Anthracene
AR	Artemis road
ATN	Acetone
AU	Artemis Urban
BaA	benzo[a]anthracene
BaP	benzo[a]pyrene
BbF	benzo[b]fluoranthene
BE	Biodiesel-ethanol
BENZ	Benzaldehyde
BghiP	benzo[ghi]perylene
BkF	benzo[k]fluoranthene
BMEP	brake mean effective pressure, N/m^2
BTDC	before top dead centre
BTX	Benzene, toluene and xylene
BUTD	Butadiene
BUTY	Butyraldehyde
CHR	Chrysene
CR	Compression ratio
CRO	Crotonaldehyde
DBA	dibenzo[a,h]anthracene
dBENZ	2,5-dimethyl benzaldehyde
DI	Direct injection
DME	dimethyl ether
DOC	Diesel oxidation catalyst
DPF	Diesel particulate filter
eBEN	ethyl benzene
FL	Fluoranthene
Flu	Fluorine
FOR	Formaldehyde
F-T	Fischer-Tropsch
GEM	Glycerol based ethyl mixture
HC	Hydrocarbon
HEX	Hexaldehyde
HMW	High molecular weight
LMW	Low molecular weight
MAH	Monocyclic aromatic hydrocarbon
MEK	Methyl ethyl ketone
MET	Methacrolein
MMW	Medium molecular weight
NaP	Naphthalene
NEDC	New European driving cycle
NO_x	Nitrogen oxides
PA	Phenanthrene
PAH	Polyaromatic hydrocarbons
PM	Particulate matter
PME	Palm based methyl ester
ppbv	Propionaldehyde
PRO	Propionaldehyde
Pyr	Pyrene
RME	Rapeseed methyl ester
SME	Soybean methyl ester
SOF	Soluble organic fraction
SUME	Sunflower methyl ester
tMBEN	tri-methyl benzene
TPO	Tyre pyrolysis oil
TOL	Tolualdehyde
UFOME	used frying oil based methyl ester
ULSD	Ultra low sulphur diesel
VAL	Valeraldehyde
WCO	Waste cooking oil

conventional diesel [1,2]. A long fatty acid chain of methyl/ethyl ester extracted from organic products like animal fat [3–6], waste cooking oil [7–12] vegetable oil [13–16] is called biodiesel. Some of the most popular methods to prepare biodiesel are micro-emulsions, thermal cracking (pyrolysis), trans-esterification [17–20] etc. The concept of biodiesel dates back to the 19th century; wherein inventor Rudolf Christian Karl Diesel ran an engine with peanut oil only [2]. Subsequently, many more oils were discovered to replace diesel from compression ignition (*CI*) engines. More than 350 oilseeds crops have been identified that can be used to prepare biodiesel [26,108]. A very important advantage of biodiesel is that it is eco-friendly. Biodiesel is better lubricant as compared to conventional fuels [21–23]. However, deposit formation, material degradation (plugging of filters) depends mainly on their degradability, impurities (glycerol content), cold flow properties, long term endurance tests and ether quality specification [24,25] need to be studied. There are three categories of sources from which biodiesel can be obtained [26], i.e., First generation (edible oils), second generation (non-edible) and third generation (microalgae).

Today, air pollution is a major issue as the main pollutants in today's environment are internal combustion (IC) engine exhausts [27] and hence, the automobile industries are focused on developing cleaner transport systems that give at least the same amount of efficiency as conventional fuels and do not cause any more pollution than what is already present. This finally leads us to the study of emission characteristics of biodiesels, since they are the single most important contender in the area of future fuels. A lot of literature is available on regulated emissions of biodiesels and its diesel blends [28–31]. In general, a large number of authors found remarkable reduction in regulated emissions like *HC*, smoke, *PM, CO*, etc., except nitrogen oxide (NO_x), by using biodiesel and its diesel blends [3,32–35]. NO_x emissions have a very different behaviour and the reasons associated for the same are operating conditions, automobile technology and fuel properties [36,37]. Apart from regulated tail pipe emissions of diesel engine, United States Environmental Protection Agency (*US EPA*) has considered the unregulated emissions such as carbonyls, *PAHs* etc. to be of toxicological consequence [38]. Some other organisations such as World Health Organisation (*WHO*), National Institute for Occupational Safety and Health (*NIOSH*), US National Toxicology Programme and International Agency for Research on Cancer (*IARC*) have also classified diesel exhausts as hazardous for human and environmental health [39–41]. The different categories under which the unregulated emissions have been grouped are: carbonyl compounds, mono-aromatic hydrocarbons (*MAHs*), polycyclic aromatic hydrocarbons (*PAHs*), nitro-*PAHs*, oxy-*PAHs*, etc. Eleven compounds were categorised by *EPA* as toxic for human and environmental health: 1,3 butadiene, *ACE, ACR*, benzene, ethyl benzene (*eBEN*), formaldehyde, n-hexane, naphthalene (*NAP*), toluene, xylene and styrene.

Carbonyl compounds are a category of organic compounds that contain the functional group $>C=O$ in their structure. They come under the category of toxic pollutants and are responsible for smog formation. They are also found in the atmosphere as a part of the ozone cycle. The most abundant carbonyls are *FOR*, *ACE* and