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Analysis of Selective Petrochemicals: A Case Study of the Houston Texas Metropolitan Area

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ANALYSIS OF SELECTIVE PETROCHEMICALS: A CASE STUDY OF THE HOUSTON TEXAS METROPOLITAN AREA

THESIS

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ANALYSIS OF SELECTIVE PETROCHEMICALS: A CASE STUDY OF THE HOUSTON TEXAS METROPOLITAN AREA

THESIS

Presented in Partial Fulfillment of the Requirements for the Master of Science Degree in the Graduate School of Texas Southern University

By
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Texas Southern University
2009

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ANALYSIS OF SELECTIVE PETROCHEMICALS: A CASE STUDY OF THE HOUSTON TEXAS METROPOLITAN AREA.

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With an increasing focus on environmental issues, a concentration on petrochemicals and their importance in commerce along with the role they play towards the issues affecting the ecosystem is a dominant topic of debate.

One major product of crude oil is petroleum, which continues to play an important role in the social, economic, and political history of the United States and the world.

Petroleum is a very complex mixture of many hydrocarbons. There are varieties of petroleum products, each of which has its own unique mix of molecules, which delineate its physical and chemical properties.

Houston happens to be one of the top cities in the United States with the worst air quality. Major sources of air pollution are attributed to emissions given off because of human actions ranging from industrial activities to on road mobile emissions.

The main goal of this project was to provide scientific reasoning for the proof that alternative fuel sources will ensure a safer and more secure environment.

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12/15/09

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My interest and involvement with Petrochemicals began on the summer of 2008, when I started working with Dr, Ford.

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Most importantly, I would like to thank my friend, and classmate Jamie Renfro-Dooley, who not only proof read my work, but help guide me to the end of this study.

DEDICATION

I dedicate this work to my parents.

Chapter 1

INTRODUCTION

Petroleum plays a very important role in the social, economic, and political history of the World and the United States. According to the Department of Energy (DOT 1998) approximately 38% (300,000) of the 800,000 shipments of hazardous materials made in 1998, were petroleum in nature.

As seen in Figure 1 below, ExxonMobil (exxonmobil.com) suggests that by the year 2030, our major source of energy will still come from petroleum.

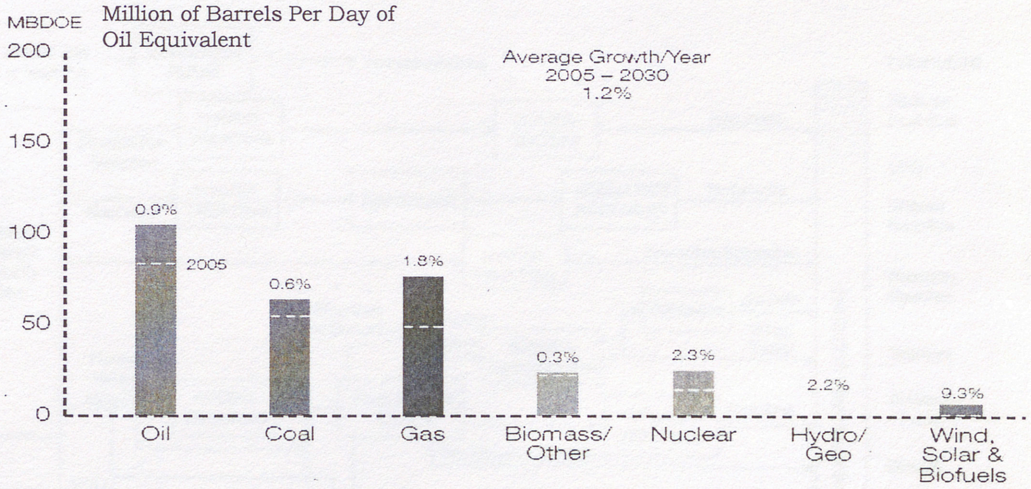


Figure 1- World Energy Consumptions by fuel types (exxonmobil.com)

Petroleum consists mainly of crude oil and natural gas (Hyne, 2001). It is a very complex mixture of many hydrocarbons, some of which include aliphatics, aromatics and asphaltenes as enumerated by the American Society for Testing and Materials [ASTM] D439 method (1983).

The physical and chemical properties of various petroleum products are defined by their unique molecular hydrocarbon content mixture, in that the percentage compositions of hydrocarbons in individual petroleum products differ among oil fields. For example, the proportional contents can range from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils (Hyne, 2001; ASTM D439, 1983)

Petroleum Refining Process

The process of petroleum refining is a very complex one, with the products generated at the end being an assorted line-up of petrochemical products ranging from automotive fuels to grease. See Figure 2 below.

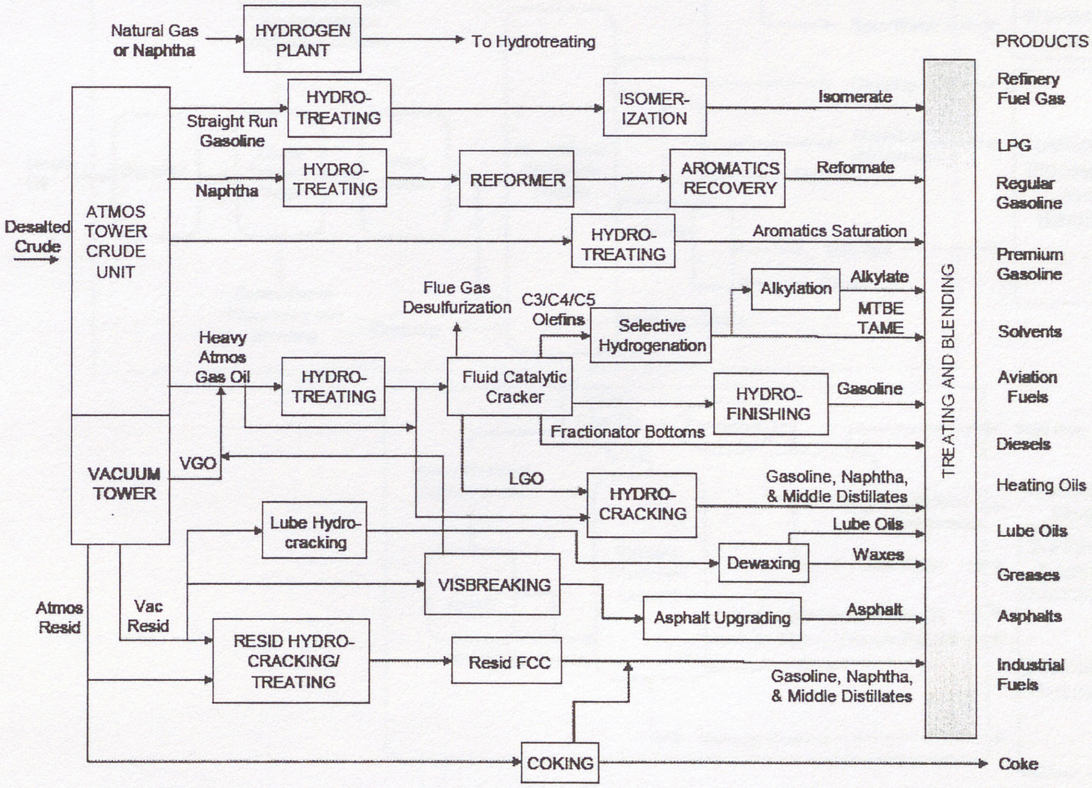


Figure 2- Diagrammatic description of petroleum refining process (DOE, 1998).

According to the Department of Energy (DOE, 1998) there are five significant procedures which are required for the complete refining of petroleum. These procedures are discussed below in sequential order.

1. **Atmospheric and Vacuum Crude Distillation**-Are the most critical steps, which separates pure oil into fractions based on boiling points of the hydrocarbons. Atmospheric Crude Distillation is carried out on lighter crude material with boiling points less than750^{o}F, and that of Vacuum is carried out on heavier crude materials which have boiling temperature higher than750^{o}F. (DOE,1998) Figure 3, illustrates further the processes of Atmospheric and Vacuum Crude Distillation

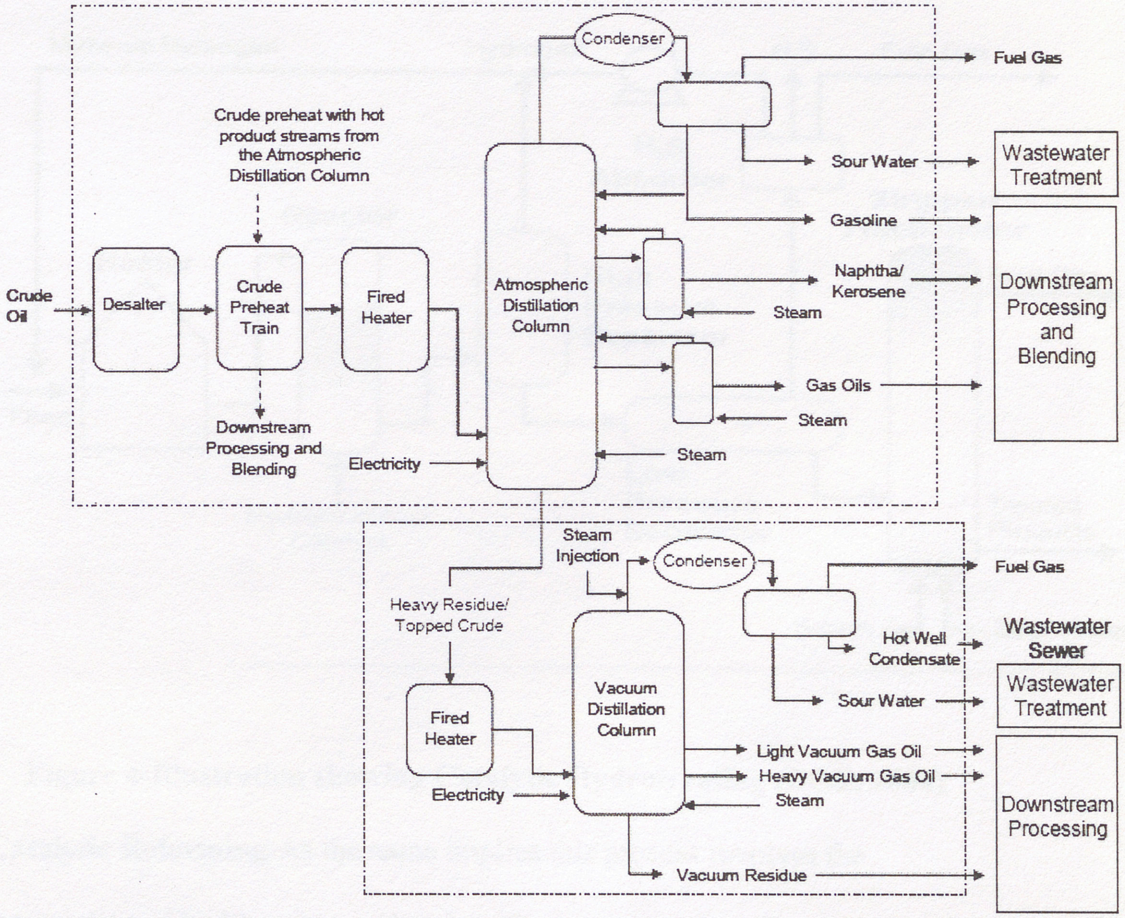


Figure 3- Flow diagram showing Atmospheric and Vacuum Crude Oil Distillation (DOE 1998)

2. **Fluid Catalytic Cracking [FCC]**-This process converts heavy oils into more valuable gasoline and lighter products. According to McKetta (1993), because of the increased demand for higher octane gasoline thermal cracking was replaced with FCC. The carbonium ions formed during the thermal cracking process can be used to increase octane number through a proton-shift and carbon-carbon emission during the process of FCC.

3. **Catalytic Hydrotreating** – As seen in Figure 4 this process is responsible for stabilizing petroleum products. During this process, sulfur and nitrogen are removed and the heavy olefins are saturated with hydrogen to produce paraffins.

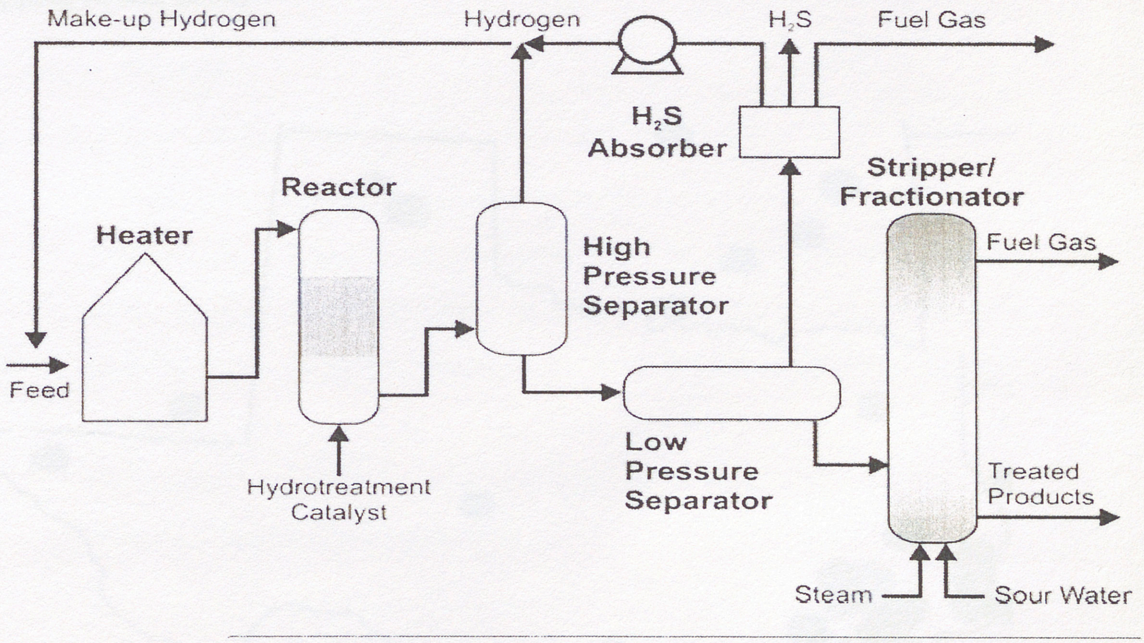


Figure 4-Illustration showing Catalytic Hydrotreating (DOE, 2004)

4 **Catalytic Reforming**-As the name implies this process involves the reconstructing of hydrocarbon molecules. The heavy pure gasoline and naphtha are converted into high-octane gasoline blending components (DOE, 2004).

5 **Alkylation**- This procedure links two or more hydrocarbon molecules to form larger ones. There are two types of alkylation, which addresses the issue of temperature. The sulfuric acid –based (H_2SO_4) alkylation is used on lighter compounds which boil at a temperature range of 40-50°F, while the hydrofluoric acid-based alkylation process involves heavier compounds which boil at higher temperatures between 70-100°F.

Hyne (2001) suggests that, the above five mentioned processes make up approximately 70% of the energy utilization by the refining industry.

There are currently 26 refineries operating in Texas (Figure. 5), with most of them located along the Golf Coast for easy access to sea transportation and shipping (DOE, 2004)

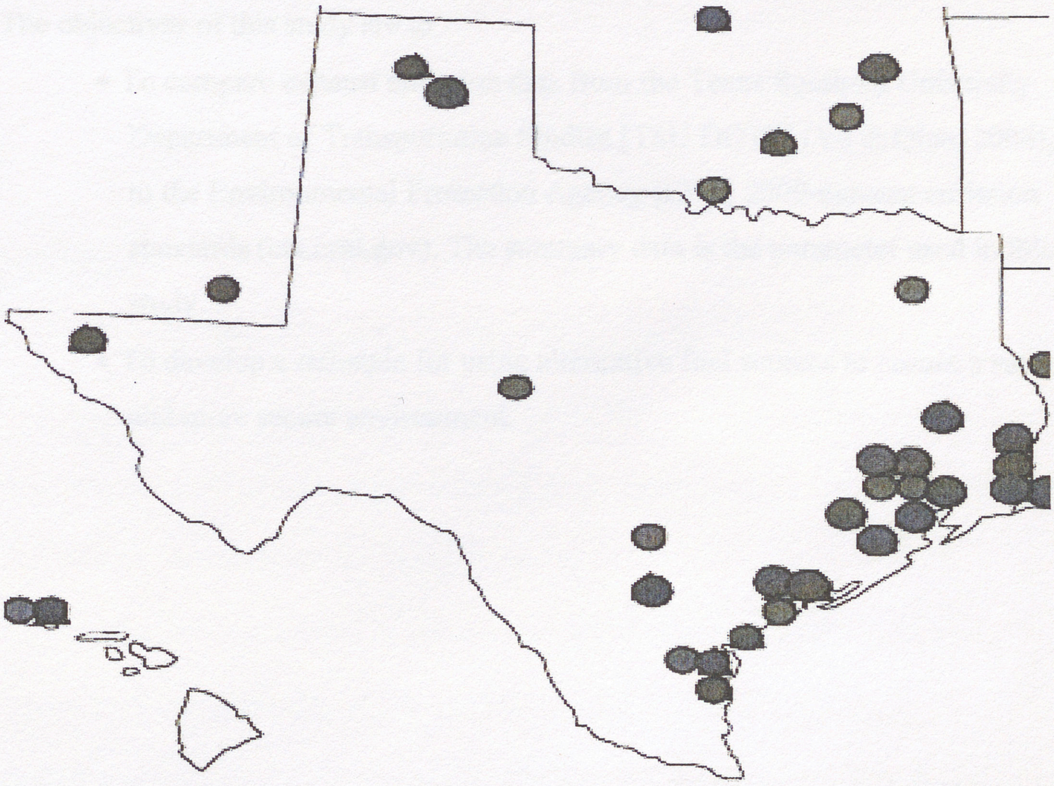


Figure 5- Geographical locations of refineries in Texas (DOE, 2004)

As seen in Table 1 below, of the 18 million barrels of crude oil distilled per day in the U.S., Texas accounts for about 870,258 barrels per day (DOE, 2004).

Houston also happens to be in the top tier of cities in the United States with poor air quality. The sources of air pollution in Houston are attributed to emissions resulting from human actions ranging from industrial activities to combustion of fuels by on road mobile sources.

The goal of this case study is to provide scientific reasoning for the proof that alternative fuel sources will ensure a safer and more secure environment.

Objectives of Study

The objectives of this study are to

- To compare exhaust emission data from the Texas Southern University Department of Transportation Studies [TSU DOTS] (Yu & Qiao, 2004), to the Environmental Protection Agency [EPA] 2009-exhaust emission standards (cta.ornl.gov). The summary data is the parameter used in this study.
- To develop a rationale for using alternative fuel sources to ensure a safer and more secure environment.

Chapter 2

LITERATURE REVIEW

Every refinery has it own distinguishing crude oil feedstock from which it obtains its unique petroleum products. However the combustion process of these products yield similar emissions of pollutants which affect the environment.(McKetta, 1993)

For the purpose of this study, the researcher looked at 2 major petroleum products as well as the alternative fuel source currently being used for powering on road mobile sources. These three products include:

1. Gasoline
2. Diesel
3. Biofuel

Gasoline

Brief History: Gasoline was first introduced in the early 20th century as a simple distillate of petroleum (Edgar, 1927). However, with swift growth and improvements in the automobile industry, more appropriate petroleum products to help the car runner faster and better were required.

The gasoline we use to fuel our cars today has come a very long way. Midgley (1989) mentions, that in the 1920s when it first was introduced, the typical gasoline octane number ranged from 40-60 and the fuel had high sulfur content. By the early 1930s, the petroleum industry realized that the large

hydrocarbon molecules present in the gasoline was seriously affecting the octane number. In the mid 1940s, catalytic

cracking was introduced, which evolved to provide consumers with good octane levels of gasoline. During 1950s, the demand for gasoline with lower sulfur content, higher octane rating, and vapor pressure levels increased.

Due to known health concerns associated with lead in gasoline identified through epidemiological and toxicological studies, unleaded gasoline was introduced in 1970, with promises that this product will not only protect exhaust catalyst but also the environment and human health (Hutcheson, 2000).

The Clean Air Act (CAA), introduced in 1990 was to enforce stringent regulations on fuel specification, in order to protect the environment (Gibbs, 1990; epa.gov/caa). The CAA was able to cause a fall in vapor pressure of gasoline, not so much the emissions as we will see in later discussions

Gasoline Octane Number: The most important gasoline parameter is its octane number which is a measure of the antiknock performance of gasoline. Antiknock agents are the driving force behind the octane quality of the different gasoline grade, in that by increasing the addition of antiknock agents [oxygenates] will cause an increase in the performance of a gasoline grade(Silva et al.,2005). Octane number is also the property that distinguishes premium gasoline from regular gasoline and other grades. On average **premium gasoline**, octane number is estimated to be about 91-92, and that of **regular gasoline** is about 87-89. In western rocky mountain areas, the octane number is about two numbers lower, because of the effects that thin air has on internal combustion (Al-Hassan, 2003)

The octane number does not indicate how much fuel power is delivered, because all grades of gasoline contain roughly the same amount of heat energy, instead a higher octane number simply means higher antiknock performance. Most cars are built to run on regular gasoline however, high performance vehicles for e.g. sports cars, often require higher grade, simply because their engines are designed for higher compression. Higher compression requires a higher octane rating, so that the fuel does not ignite before the piston reaches Top Dead Centre, which could cause the engine to knock if regular gasoline is used. In the same way, using high-octane gasoline in cars designed for regular really serves no benefit to the owner, except rapid combustion of their money. To know what type of gasoline is best for one's car, the owner's manual references the manufacturer's recommended grade of gasoline (Marshall & Owen, 1995)

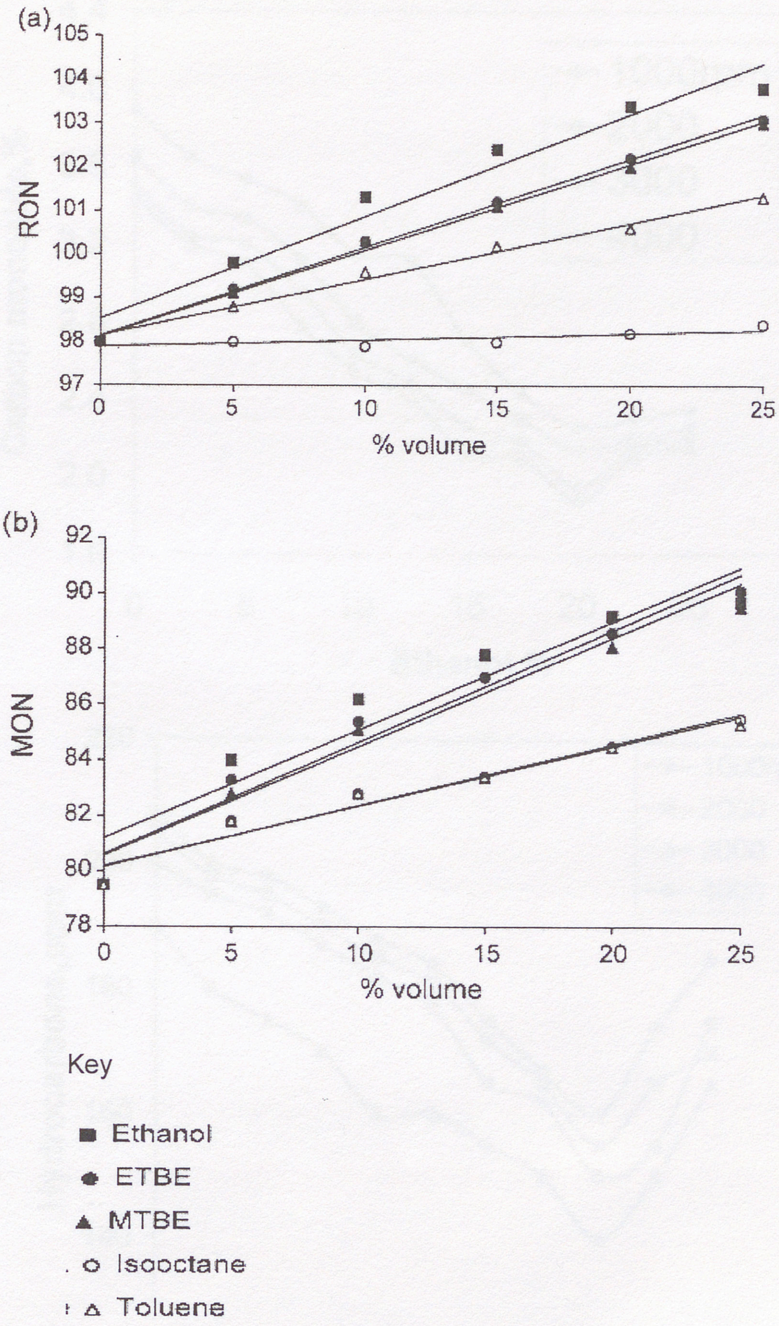
Tetra-ethyl-lead (TEL) developed in the early 1920s was the first commercially successful antiknock agent. However due to it's highly toxic and poisonous effect (very high lead content) it had to be withdrawn.

Methyl t-butyl ether (MTBE) a lead free antiknock agent was introduced in 1970 with promises of less toxic effects and higher-octane quality coupled with low volatility and easy solubility in gasoline. The report of Keller et al. (1998), suggests leakage of gasoline from underground storage tanks resulted in the detection of MTBE in drinking water of several urban areas around the state of California, which prompted the fading out of this product from California gasoline. With inconclusive reviews, that this particular oxygenate may have carcinogenic effects (epa.gov/mtbe), other states around the country decided to follow California and stop the use of MTBE.

A more environmentally friendly Ethanol was the main additive used to replace MTBE. Research carried out by Hutcherson (2000) to investigate the effect of ethanol in gasoline, reported that not only did the addition of Ethanol in gasoline cause an increase in gasoline octane number but also dissolved in water does not pose as much a threat as dissolved MTBE. A similar study carried out by Silva et al.,(2005) also report that percentage increase of ethanol in regular-unleaded gasoline increased the Research Octane number[RON] when the engine of the vehicle was driving on a highway; it also increased the Motor Octane Number[MON] when the engine was driving up hill(Figure 6). Figure 7 illustrates a similar study done by Al-Hassan (2003), using ethanol-unleaded gasoline blends showed that at different revolutions per minute (rpm) of a car engine, increased percentage addition of ethanol in gasoline caused a decrease in exhaust emission of Carbon Monoxide [CO] and Hydrocarbons.

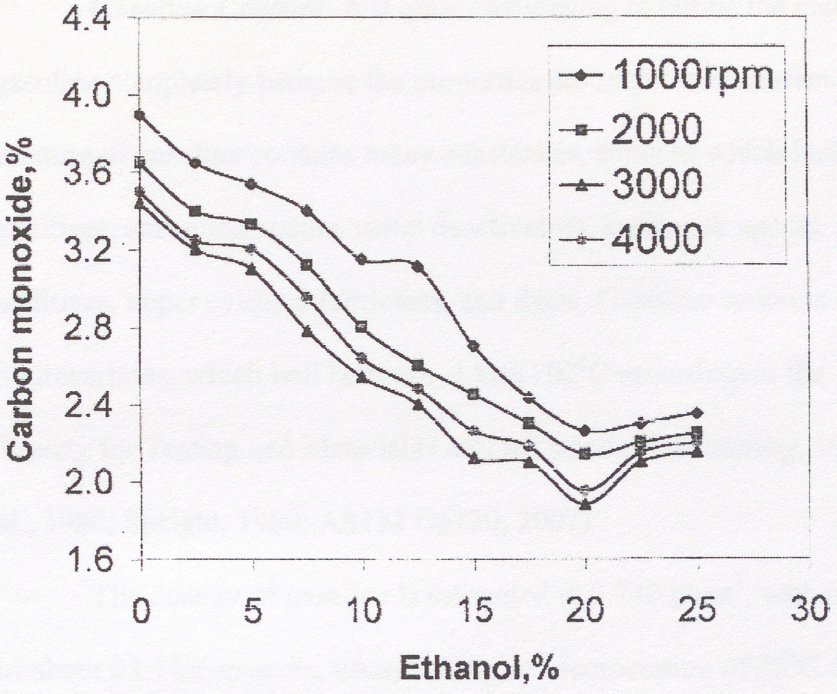
These studies indicate that Ethanol is a safer replacement for MTBE in that ethanol works by increasing octane number so extra compounds are not needed to boost the number, and is also environmentally and health friendly because it reduces the amount of pollutants emitted.

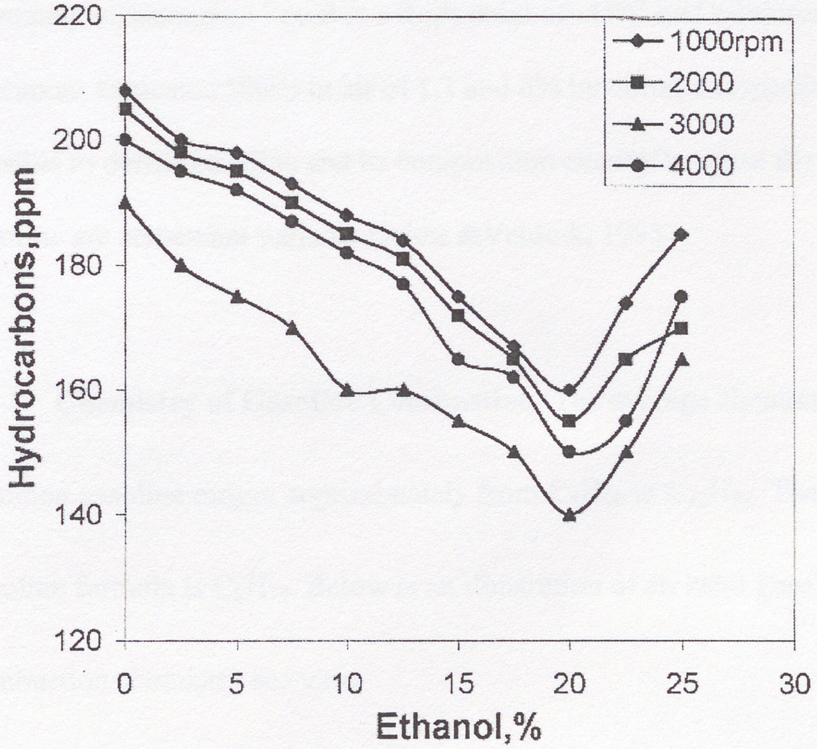
Ethanol is one of the major biofuels currently being explored as an alternative for fossil fuel; and this is discussed further later in this chapter.



Note-Isooctane and Toluene are non-additives used as controls in this experiment

Figure 6- Effects of additives on RON and MON (Silva et al., 2005).





Key

ppm- Parts per Million

Figure 7-Effects of Ethanol addition on exhaust emissions of Carbon Monoxide (CO) and Hydrocarbons (HC), (Al-Hassan, 2003).

Gasoline Content: It is quite challenging to define the composition of gasoline completely because the properties are rather inconsistent. The complex mixture of gasoline contains many substances, some of which include pre-ignition additives, anti-icing agents, metal deactivators, antiknock agents, antirust additives, upper cylinder lubricants, and dyes. Gasoline contains over 500 hydrocarbons, which boil between -1 and 202°C according to the American Society for Testing and Materials (ASTM) standard (Kettering, 1994; Bingham et al., 1980; Speight, 1980; ASTM D6730, 2007)

The density of gasoline is estimated at 0.730 g/cm^3, with a vapor pressure of about 93.3 kilopascals, when boiling at a temperature of 25°C. It is an extremely inflammable liquid at a flash point of -45°C and minimum and maximum explosion limits in air of 1.3 and 6% by volume respectively. It is not possible to define gasoline and its composition exactly because the properties of gasoline are somewhat variable (Jeltes &Veldink, 1995)

Chemistry of Gasoline Combustion: The average chemical formula for common gasoline ranges approximately from C_4H_{10} to $C_{12}H_{26}$. The typical gasoline formula is C_8H_{18}. Below is an illustration of an ideal gasoline combustion chemistry scenario

1. $C_8H_{18} + 25/2O_2$ + Heat → $8CO_2$ + $9H_2O$ + Heat [Complete Combustion]

2. $C_8H_{18} + 13O_2$ + Heat → $8CO$ + $9H_2O$ + Heat [Incomplete Combustion]

In reality the process of gasoline combustion, is not as clean as stated above this is because gasoline is a mixture of several hydrocarbon materials,

additives and other agents introduced during the refining process in order to enhance the performance of the end products and/or to comply with environmental regulations. Conditions like temperature, pressure and catalyst also play a role in the end product formed from gasoline combustion. This makes having a specific reaction without knowing what the materials are impossible. As stated above in an ideal simple combustion scenario the reaction of hydrocarbons e.g. C_{8H18} with atmospheric O_2 will yield carbon dioxide (CO_2) and water (H_2O) in a complete combustion, and carbon monoxide (CO) and water (H_2O) in an incomplete combustion, but in reality the combustion process is never complete hence more CO is produced. The other emissions such as oxides of nitrogen (NOx), and sulfur oxide (SO)arise from combustion of naturally occurring nitrogen and sulfur compounds in crude oil. Several studies do prove that the combustion of gasoline does result in some form of pollutant emission. For example research conducted by Hutcheson (2000) illustrates that the transition from leaded to unleaded gasoline on the plus side meant no more lead exposure, increased vapor pressure and constant sulfur and olefins content. However on the negative side the removal of lead meant increased aromatic content to boost the octane number, which results in increased benzene and formaldehyde emissions, another recognized set of toxic compounds which also contribute to photochemical pollution, and also increased vapor pressure (Hutcheson, 2000). Similar studies carried out by Hammerle using the Methylcyclopentadienyl Manganese Tricarbonyl (MMT) an organic lead-free manganese fuel additive designed to boost gasoline octane number, suggest that there is an increase in particulate emissions of on road mobile sources which is primarily due manganese oxide emissions. It was also observed that MMT increased emissions

of Hydrocarbon (HC), Carbon Monoxide (CO), and Oxides of Nitrogen (NOx) (as cited by Silva et al., 2005).

In another study carried out by Battin (2008), the alkanes released during the combustion of unleaded regular gasoline at temperatures higher than 120Kelvin [K] react with atmospheric O_2 to for, alkyl and hydroperoxy radicals. Also at low temperature ranges between 500-600K, the alkyl radical react with atmospheric O_2 to form peroxalkyl radical, which in turn form peroxide species which are responsible for Ozone formation and also thought to have high affinity for haem in haemoglobin (Morris et al., 1995).

The studies mentioned above all point to one problem, which is that regardless of the type of gasoline used, its combustion will always result in the emissions of pollutants, which in turn affect the environment.

Diesel

Brief History: The first diesel engine was originally designed by a German engineer Rudolf Diesel, in 1893, using coal dust as his fuel. However, this diesel driven machine was a stationary one (Wellington & Asmus, 1995)

According to studies carried out by Wellington and Asmus (1995) the first locomotive diesel engine, an oil-tanker ship called "Vandal", was built around 1903, in Sormovo, Russia. Mercedes Benz decided to experiment further with diesel engine in 1922, and one product from their trails was an agricultural tractor, the first vehicle powered by diesel, which was later made available to the public in 1924. Later in 1953, Mercedes Benz would go on to create the "Turbo Diesel Truck" that would be mass-produced by Volvo the following year. The French company Peugeot introduced the Peugeot 204 the first small car with a front wheel drive and slating mounted diesel engine (Marshall & Owen, 1995).

Contents of Diesel: Diesel also known as petrodiesel generally consists of middle end distillates of crude oil fractions with boiling points between 160-371°C, according to ASTM standards (ASTM D975-09b, 2009). The hydrocarbon chains in diesel tend to be a little longer than that of gasoline, the alkanes make up 60-90% of the hydrocarbons, aromatics about 10-30%, and alkenes make up less than 5%(ASTM D975-09b, 2009)

Diesel density is estimated at 0.85 g/cm^3, with a vapor pressure of about 0.053 kilopascals. It is an inflammable liquid at a flash point of >52°C and minimum and maximum explosion limits in air of 0.3% and 10% by volume, respectively (ASTM D975-09b, 2009).

Diesel Sulfur Rating: Oxides of Sulfur is listed as one of the five criteria pollutants by the EPA (epa.gov/air). Crude oil naturally contains sulfur, which is passed on into refined crude products especially diesel. Several studies indicate that compounds of sulfur have toxic environmental and health effects when released into the air during combustion. One of such studies carried out by Komarnisky et al. (2003) suggests that sulfur oxides present in sediments of diesel emission represent a potential risk to human health due to the possibility of their mobilization and amplification through the food chain.

Another study observed that on contact with moist membrane SO_2 form sulfuric acid [H_2SO_4], which is responsible for severe irritant effects on the eyes, mucous membrane and skin. H_2SO_4 also depresses pulmonary particle clearance, the major protective mechanism in lungs (Amdur, 1989).

In August 2006 the Environmental Protection Agency began leading the transition program requiring all on-road vehicle to switch from low-sulfur diesel (LSD) containing about 500 parts per million (ppm) to ULSD which contains less than 15 ppm of sulfur, The carefully designed program was created to reduce the toxicity of sulfur emission in the environment (epa.gov/oms.). However, just as in the case of gasoline transition diesel desulfurization meant a decrease in its lubricity, hence additives have to be added to the product to balance the sulfur taken out.

Chemistry of Diesel Combustion: The average chemical formula for common diesel ranges approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. An ideal Diesel combustion chemistry scenario would be as follows

1. $C_{15}H_{28} + 29O_2$ + Heat → $15CO_2 + 28H_2O$ + Heat [Complete Combustion]

2. $C_{15}H_{28} + 43/2O_2$ + Heat → $15CO + 28H_2O$ + Heat [Incomplete Combustion]

The equations above show an ideal simple combustion scenario where diesel represented as $C_{15}H_{28}$ reacts with atmospheric O_2 to yield CO_2 and H_2O in a complete combustion, and CO with H_2O in an incomplete combustion. Just like in the case of gasoline combustion, the process of diesel combustion is not as clean as stated above this is because diesel also contains a mixture of several hydrocarbon materials, additives and other agents as well. Researches nevertheless do prove that the combustion of diesel does cause emission of pollutants like soot, sulfites. One of such research was that of Flyn et al (1999) which showed that diffusion controlled combustion characteristics of diesel engines generates significant levels of oxides of nitrogen (NOx) and soot emission. A similar study illustrated that Polycyclic Aromatic Hydrocarbons

(PAH), an alkylated major aromatic component of diesel fuel have a great tendency to form larger condensed aromatic structure e.g. Benzo[e]pyrene a known carcinogen during pyrolysis. The larger structures in turn are confirmed precursors in soot formation (Tancell et al., 1996).

With these findings, it is obvious that diesel combustion emissions are also responsible for environmental pollution as well as health problems.

Other forms of diesel such as Biodiesel, biomass to liquid (BTL) and gas to liquid (GTL) are currently developed and implemented in the same way as petroleum generated diesel, with results of less emissions. Details of theses alternative form of diesel are discussed under Biofuels.

The Alternative, Biofuel.

The United States accounts for almost 20% of the world's energy production and the greater part of this energy production source as mentioned earlier is from petroleum (peakoil.net). According to the Association for the Study of Peak Oil & Gas[ASPO] (peakoil.net), the highest ever oil discovery peak worldwide at 147 Gigabarrels was in 1947, and the closest we have ever come to another high peak was on 1964, with a discovery of 90 Gigabarrels. It seems that even the successful North Sea oil discoveries in the mid 1970s made no difference in any way to the clearly noticeable decline in this valuable natural resource (Figure 8).

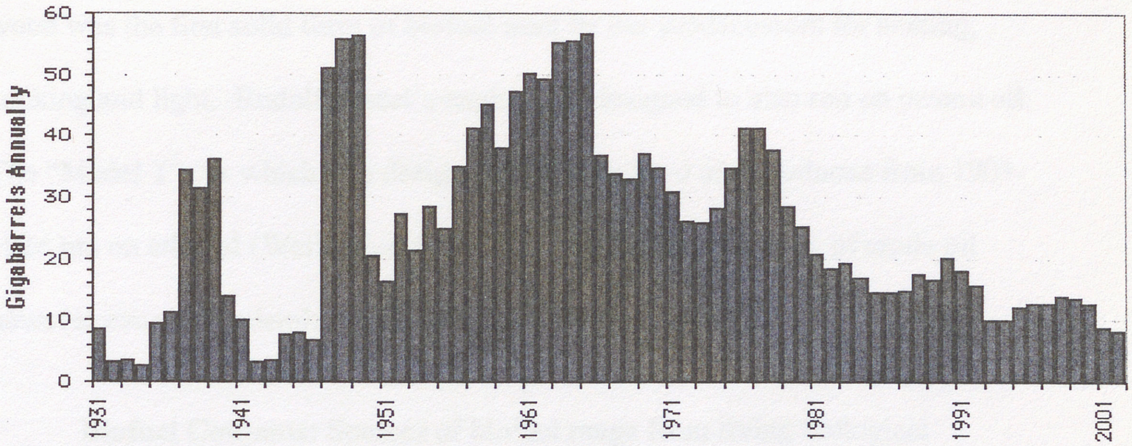


Figure 8-Crude Oil Discovery Timeline (peakoil.net)

ASPO (peakoil.net) mentions that because crude oil is an important non-renewable resource, a political-act was put in place to publish reserve data; however, that being said, reliable data of exactly how much crude oil is left worldwide are hard to come by (sierraclub.org).

With concerns that we may be running out of natural crude reserves, along with heightened awareness of the environmental impact of these petroleum products, striking progress is being made towards the creation of alternative renewable sources to help meet, the continuous increase in energy demand (Finlayson-Pitts & J. Pitts, 1993; Yunqiao et al., 2007).

Biofuel

Brief History: Biomass or Biofuel as we know it is the main alternative energy source making headlines in today's market, types of which include biodiesel, bioalcohol, and hydrogen(Yunqiao et al., 2007). Inderwildi & King (2006) claim that biofuel was first discovered when man discovered fire; in that

wood was the first solid form of biofuel used by our predecessors for heating, cooking and light. Rudolf Diesel's engine was designed to also run on peanut oil. The "Model T" car which was designed by Henry Ford and produced from 1903-1926 ran on ethanol (Wellington & Asmus, 1995). The discovery of crude oil however caused the demise in biofuel usage (Collins, 2007).

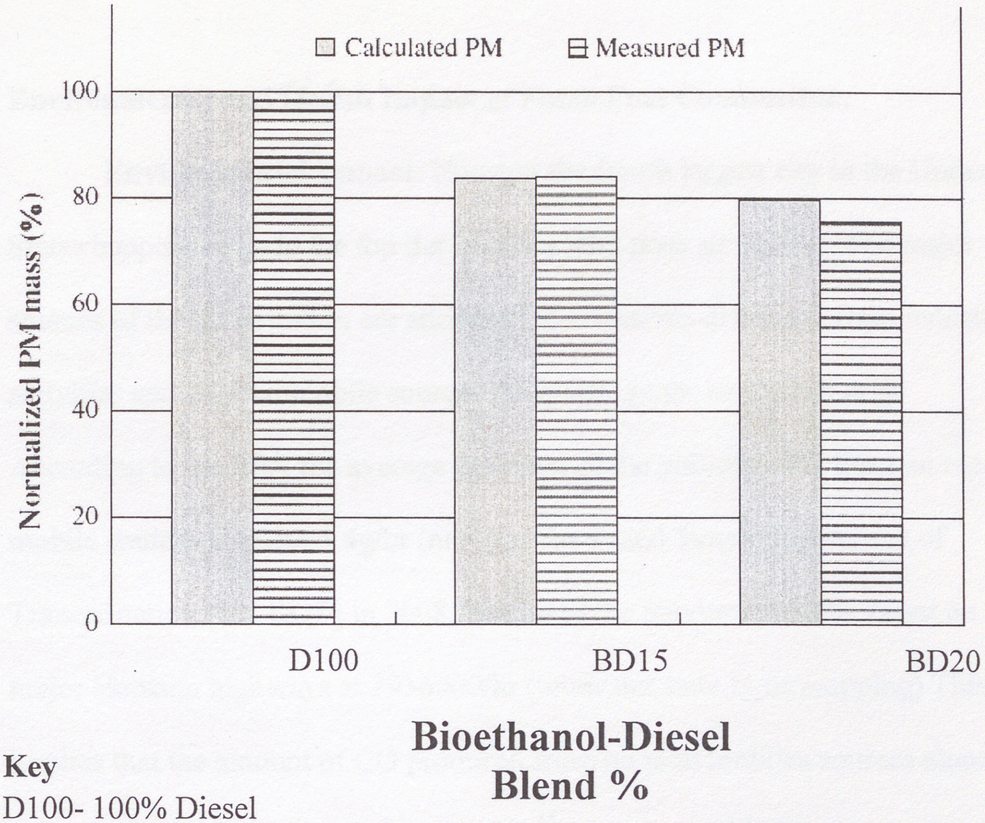
Biofuel Contents: Sources of biofuel range from living biological materials like algae to agricultural crops like corn. Biofuel is divided into three generations. By means of conventional technology, the first generation biofuel are made from vegetable oil, animal fat, sugar or starchy crops like corn. A good example of a first generation biofuel is bioethanol, the fermented product of starch. The second-generation biofuel include woody crops and grass species e.g. Lignocelluloses (Finlayson-Pitts & J. Pitts, 1993). The third generation, which was launched in 1978 and is still currently stirring up much attention, is algae generated biofuel (Yunqiao et al., 2007).

Chemistry of Biofuel Combustion: In this study bioethanol combustion was observed. The equation for the combustion of bioethanol is as follows

1. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ + Heat [Complete Combustion]
2. $C_2H_5OH + 2O_2 \rightarrow 2CO + 3H_2O$ + Heat [Incomplete Combustion]

The equations above show an ideal simple combustion scenario where C_2H_5OH reacts with atmospheric O_2 to yield CO_2 and H_2O in a complete combustion, and CO with H_2O in an incomplete combustion. As mentioned before bioethanol is ethanol fermented from glucose found in natural resources like corn. It produces enough heat to be used as a fuel for transport when combusted (bath.ac.uk). Even though technology has not found a way yet to make

it produce as much energy as per liter of gasoline or diesel, it does however have several advantages in a world where less dependability on fossil fuels in the future seems unavoidable. One of such advantages is that the CO_2 released during fermentation and combustion is said to equal the amount removed from the atmosphere, while the feedstock crop is growing, and CO emissions are much less than in the combustion of fossil fuels. Research by Al-Hassan (2003) discussed earlier on supports the claim by illustrating that ethanol-unleaded gasoline blends did reduce CO and HC emission, but increased CO_2 emissions which can be used for feedstock growth (Figure 7). Studies carried out by Chang et al., (1991) suggest that the reason for the high CO_2 emissions is that they have lower energy content and therefore consume more fuel to travel the same distance as fossil fuels (Table 2). Illustrated in Figure 9 is another research by Hwanam and Byungchul (2010) claiming that Bioethanol blended diesel fuel reduced the amount of Particulate Matter emissions.



Key

D100- 100% Diesel

BD15-15% Bioethanol blended diesel

BD20- 20% Bioethanol blended diesel

Figure 9- The effects of Bioethanol blended diesel fuels on Particulate Matter (PM) emissions (Hwanam & Byungchul, 2010)

Fuel	BTU/gallon	Miles/gallon	CO_2 (g $mile^{-1}$)
Gasoline	115,000	34	315
Diesel	102,000–156,000	39–48	315–252
Methanol	56,000	22	272
Ethanol	76,000	28	243
Methane	20,000[a]	8	301
Propane	94,000[b]	31	229

Key

BTU-British Thermal Unit also known as joules
g $mile^{-1}$ –grams per mile

Table 2- Energy Content and CO2 emissions of different fuels (Chang et al., 1991)

Environmental and Health Impact of Fossil Fuel Combustion.

Environmental Impact: Houston the fourth largest city in the United States happens to be in the top tier of cities with poor air quality. The major sources of the air pollution are attributed to emissions discharge from industrial activities and on road mobile sources (tceq.state.tx.us; serriaclub.org). According to the EPA the average emission of the pollutant CO from on road mobile sources is about 5.4g/hr (nrel.gov/docs) and Texas Department of Transportation [TX DOT] in 2008, estimated the maximum traffic count on all major Houston highways at 2936000/hr (www.dot.state.tx.us/mapping) This implies that the amount of CO produced from on road mobiles sources alone in the year 2008 was in the bracket of $1.39e^{11}$grams/hr, making it evident that the emissions from on road mobile sources does play a major role in the poor quality of the city. One major area of air pollution that is of great concern is the aspect of Ozone standard. The Houston-Galveston area is a region where the National Ambient Air Quality Standard (NAAQS) for ozone is often violated (epa.gov/caa). In March of 2007, the EPA imposed federal regulations for ground level ozone, which the Houston-Galveston ozone violating regions had to obey. Failing to comply puts more than 4 billion dollars in federal funds at risk annually (epa.gov/caa; Yu & Qiao, 2004). The formation of Ozone is a series of complex cycles involving carbon monoxide and volatile organic compounds, released as a result of fuel combustion, being oxidized into to water vapor and carbon dioxide (Finlayson-Pitts & J. Pitts, 1993). The five step reaction processes involving Ozone formation are described below using carbon monoxide which is formed from the combustion of hydrocarbons from fuel sources. Although not covered in

this review, the reaction process involving volatile organic compound in the formation of Ozone is similar to that of carbon monoxide.

1. $OH + CO \rightarrow H + CO_2$. The oxidizing process here involves a reaction between CO and a hydroxyl radical OH to form CO_2 and Hydrogen
2. $H + O_2 \rightarrow HO_2$. The hydrogen formed from the oxidation process above rapidly reacts with oxygen in the atmosphere to form protonated superoxide.
3. $HO_2 + NO \rightarrow OH + NO$ The protonated superoxide then go on to react with NO to give NO_x
4. $NO_x + hv \rightarrow NO + O$. The NO_x is broken down by photons to produce atomic oxygen
5. $O + O_2 \rightarrow O_3$. Atomic oxygen reacts with atmospheric oxygen to generate ozone also known as smog.

Ozone or smog as it is sometimes called have been linked to visibility impairment at times of the day, and in high concentrations can cause plant damage during their growth period.

Health Impacts: In terms of fuel combustion impact on health, CO is known to be a toxic compound, which can cause headaches, dizziness, weakness, vomiting and in extreme cases death when inhaled in high levels. In a study by Poon et al. (2007) potential health risk involved in exposure to soot from diesel combustion was illustrated in their experiment on male rats which developed hyaline-droplet nephropathy [a condition that renders globulins resistant to digestion by lysosomal protease] after 4 weeks of exposure to soot from Low

Sulfur Diesel combustion. Another study by Lewtas (2007) observed that soot a particular combustion product of diesel contains mutagenic particles, which were identified as chemical carcinogens.

According to EPA (epa.gov/otaq/regs) prolonged (6-8 hours) repeated exposure to ozone can cause inflammation and defense mechanism impairment of the lungs, over time this could lead to premature ageing of the lungs and/or serve chronic respiratory illnesses.

Chapter 3

DESIGN OF STUDY

The goal of this study is to provide scientific reasoning for the proof that alternative fuel sources will ensure a safer and more secure environment.

Using available literature, the study described the chemistry of the complete and incomplete combustion of fuels in an ideal scenario.

The study also compared emission data from the Texas Southern University Department of Transportation Studies [TSU DOTS] (Yu & Qiao, 2004) to the Environmental Protection Agency [EPA] exhaust emission standards for cars in effect in 2009 (cta.ornl.gov). According to the raw data generated by TSU DOTS research, Table 3 was created to show the summary of the amount of CO, and NOx emissions from cars. The data was compared to EPA standard emission data in Table 4, which was implemented at the beginning of 2009. This study compares the findings in Table 3 and 4. The result from this comparison is valid proof that the alternative biofuel sources are the best route to follow for a friendlier environment.

Another factor that was considered was the emissions data from transportation collected over five years as reported by the EPA (cta.ornl.gov/data). Transportation which involves fossil fuel combustion to produce exhaust emissions, accounts for the majority of CO and NOx emissions. Highway vehicles are recognized as the largest contributors to transport emissions (www.epa.gov/ttn/trends). Table 5 compares the total amount of emissions of 3 criteria pollutants contributed by emissions alone to other sources collected over 5

years by the EPA (cta.ornl.gov/data), the claim that biofuel which produces less emission is a better alternative for on road mobile sources can be supported.

The last factor considered in making a case for the switch to alternative fuels is the inconsistency in crude oil prices. The average price of a barrel of crude oil stands at $80 per barrel today, which is more than double its price in the year 2000 (eia.doe.gov). It is hoped that with advancement in technology, the minimal disadvantages associated with biofuel (Table 6) can be fixed and hence the current price of $108 per barrel of biofuel will significantly reduce over time and be able to compete with the ever-soaring price of crude oil.

Chapter 4

ANALYSIS OF DATA

Carbon Monoxide (CO) and Oxides of Nitrogen (NOx), are two of the five major pollutants listed as criteria pollutants by the EPA (epa.gov/air/criteria).

According to research carried out by the TSU DOTS, Table 3 below is the summary emission of CO, and NOx in grams per mile of all cars tested on different Houston roadways.

Sector	CO(g/mile)	NOx(g/mile)
Summary of car emissions on all roads (g/mile)	7.4959	1.8530

Table 3- Summary of CO, and NOx emission from cars on Houston roadways as analyzed by TSU DOTS (Yu & Qiao, 2004).

Table 4 below on the other hand shows the standard average emission of a car with a starting mileage of 120,000, as set by the EPA.

Sector	CO(g/mile)	NOx(g/mile)
Standard average emission (g/mile)	2.8875	0.0763

Table 4- EPA exhaust emission standard for cars with a starting mileage of 120,000, in effect in 2009 (cta.ornl.gov)

From Tables 3 and 4 it is evident that the emission from the two major criteria pollutants as tested by the TSU DOTS is far higher than the standard

average emission as set by the EPA, hence providing valid proof that the alternative biofuel is the better choice of fuel for the benefit of the environment. Figures 10 and 11, illustrate the comparison between the TSU DOTS and the EPA data. From these illustrations, it is very clear that the EPA data is the standard reference that can be used in this comparative case study. This is sound scientific evidence that emissions from cars contribute to the poor air quality in the city of Houston.

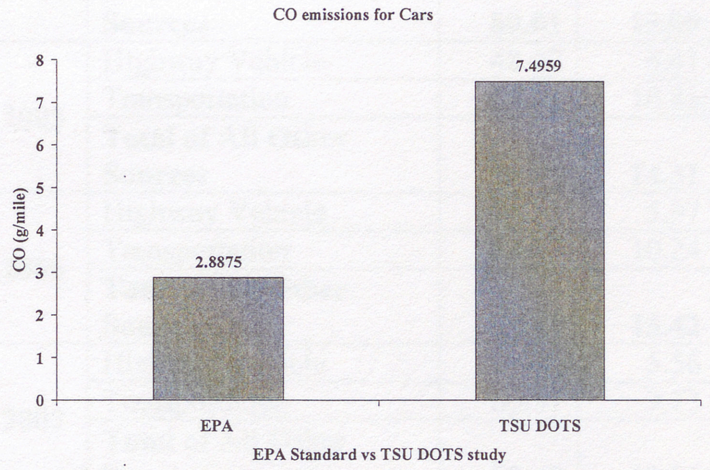


Figure 10-CO Emission for Cars (Yu & Qiao, 2004; cta.ornl.gov)

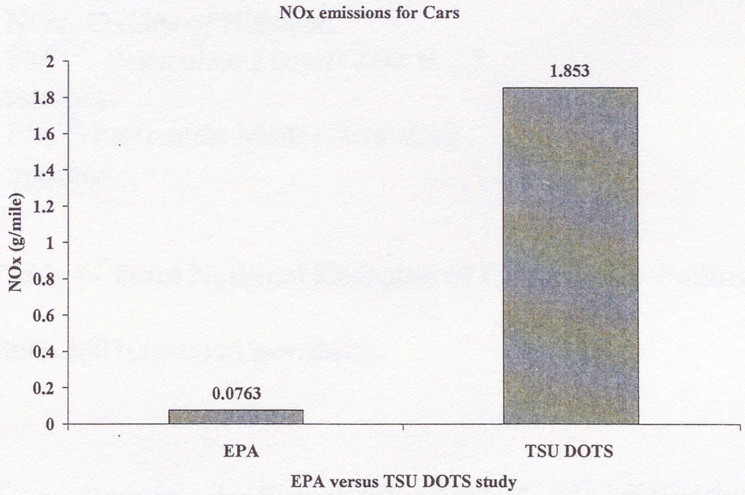


Figure 11-NOx Emission for Cars (Yu & Qiao, 2004; cta.ornl.gov)

Table 5 represents measurements made by the EPA of the total amount of emissions, of the three major criteria pollutants contributed by highway vehicles, transportation and other sources, from 2003- 2007 (cta/ornl.gov/data).

		Amount of Factor contributed (Million Short tons)			
Year	**Sector**	**CO**	**NOx**	**$PM^{-2.5}$**	**PM^{-10}**
2003	Highway Vehicle	56.47	7.38	0.141	0.2
	Transportation	78.51	11.86	0.432	0.51
	Total of All Other Sources	**84.2**	**15.85**	**5.273**	**21**
2004	Highway Vehicle	52.35	6.9	0.134	0.19
	Transportation	73.77	11.33	0.426	0.5
	Total of All Other Sources	**80.01**	**15.09**	**5.259**	**20.99**
2005	Highway Vehicle	48.22	6.41	0.127	0.18
	Transportation	69.03	10.81	0.419	0.5
	Total of All Other Sources	**75.81**	**14.31**	**5.244**	**20.97**
2006	Highway Vehicle	44.73	5.97	0.12	0.18
	Transportation	64.39	10.24	0.403	0.48
	Total of All Other Sources	**72.47**	**13.42**	**5.208**	**19.03**
2007	Highway Vehicle	41.61	5.56	0.0114	0.17
	Transportation	60.37	9.73	0.39	0.47
	Total of All Other Sources	**69.49**	**12.86**	**5.0714**	**17.07**

KEY
CO- Carbon Monoxide
NOx- Oxides of Nitrogen
$PM^{-2.5}$- Particulate Matter- Size at 2.5 microns
PM^{-10}-Particulate Matter-Size at 10 microns

Table 5- Total National Emission of Criteria Air Pollutants by Sector, for 2003-2007(cta/ornl.gov/data).

Based on the figures in the Table 5, it is evident that on road mobile sources are responsible for the high levels of CO and NOx in the atmosphere. The

emissions of the $PM^{-2.5}$ and PM^{-10} can be attributed to other sources like industrial activities.

Concerning the aspect of the price of crude oil, there has been a constant fluctuation. Figure 12 shows the cost of the price of a barrel of crude from 2000-2008.

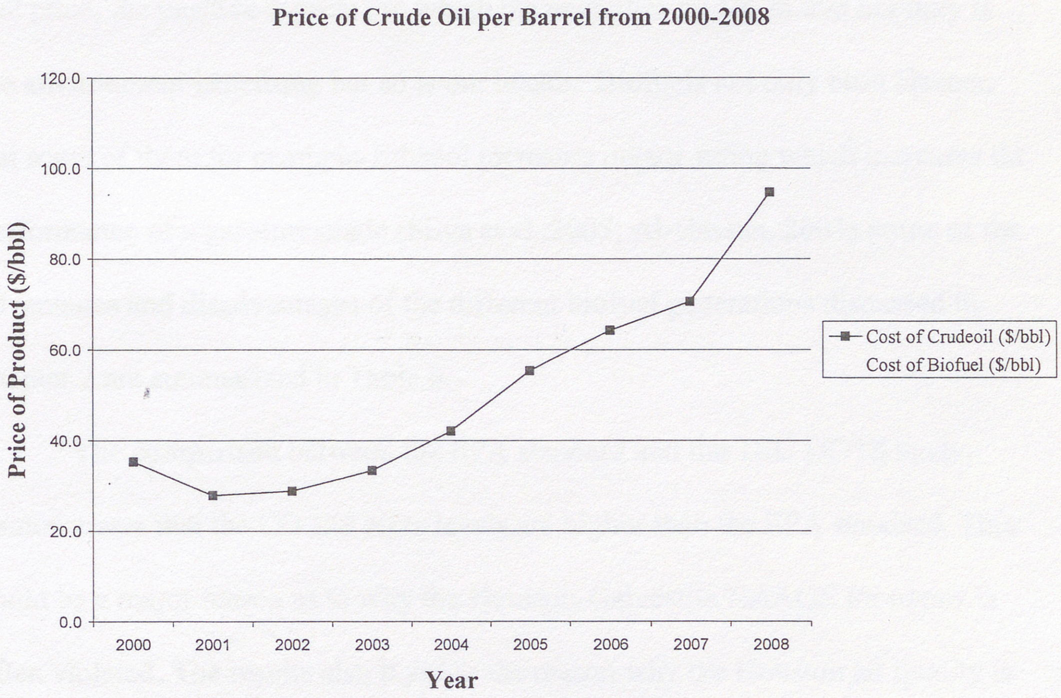


Figure 12 – Price of a barrel of Crude Oil from 2000-2008(cta/ornl.gov/data).

From this Figure, it can be seen that there is a continuous climb in the price of crude oil.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

Conclusion

Although biofuels have some disadvantages in terms of extraction process and price, the positive aspects out weigh the negatives by far, in that not only is the environment benefiting but so is our health. Biofuels not only burn cleaner, but some of them for example-Ethanol increases octane rating which increases the performance of a gasoline grade (Silva et al.,2005; Al-Hassan, 2003).Some of the advantages and disadvantages of the different biofuel generations discussed in chapter 2 are summarized in Table 6.

The comparison between the EPA standard and the TSU DOTS study, demonstrates that the CO and NOx levels are higher than the EPA standard. This could be a major reason as to why the Houston-Galveston NAAQS for ozone is often violated. The results also point to the reason why the Houston air quality is ranked as one of the worst.

Due to the fact that crude oil is a non renewable natural resource, we are not sure of how many natural crude reserves we actually have left (sierraclub.org). Also from studies and research carried out as reported in chapter 2 it is evident that emissions from the products from crude distillation, contribute to the destruction of our environment (Finlayson-Pitts & J. Pitts, 1993; Yunqiao et al., 2007). Hence, it is apparent that going green is our best bet, in that biofuels should be the main source of energy production; whether it is for heating or for powering our vehicles.

Recommendation

The recommendations, which come to mind because of this study, are detailed below.

Collaboration between the TSU DOTS and the Environmental Toxicology Program should be undertaken to analyze on road mobile source emissions using the Portable Emissions Measurement System [PEMS] (Yu & Qiao, 2004). The results can help to validate the claim that fossil fuel combustion in vehicles produces high levels of toxic emissions, which are not environmentally and health friendly.

It is also recommended that petroleum product sampler taken from refineries be analyzed for specific content and to investigate whether current fuel additives increase fuel efficiency.

It is also our duty as individuals, to find out the exact contents of the products we make use of everyday. It is also our duty to determine if they are harmful or beneficial to our health and environment; not just leaving the decision to the profiting market, who care more about the financial aspect than the environmental aspect (money.cnn.com)

Biofuel Generation	Uses	Advantages	Disadvantages
1st Generation Biofuels	Used for generating energy.	Production method is cheap Feedstock production provides job opportunities for farmers, most especially in third world countries.	The waste product is hard to dispose off, indicating that perhaps they are no better off than their fossil fuel counterpart. May alter food chain supply.
2nd Generation Biofuels	Used for heating and cooking.	They can be cultivated on degraded soil. Production method is also quite conventional. Feedstock is in abundance.	The breakdown process of cellulose in the plant specie is a meticulous one; hence, the biofuel obtained is more expensive than fossil fuels. Care has to be taken when cultivating the grass species because they tend to be invasive, which can lead to negative impacts on their surrounding environment. Wood burning increases CO_2 in the environment.
3rd Generation Biofuels	When mixed in the right proportion with petroleum products can be used as a fuel for powering automobiles.	Simple plant like organisms which have a low input, high yield capacity Their processing method can help to reduce CO2 in the environment The waste product can be used as animal feed and for the production of ethanol.	The extraction process is not only hard but also expensive.

Table 6- Some uses, advantages, and disadvantages of Biofuels.

APPENDIX A.

ORIGINAL RAW DATA TABLES.

Name of Refinery	Refining Company	Location in Texas	Atmospheric Crude Oil Dist.(bbl/d)	Meters cubes per day(m3/d)
Baytown Refinery	ExxonMobil	Baytown	557,000	88,600
Big Spring Refinery	Alon USA LP	Big Spring	61,000	9,202
Beaumont Refinery	ExxonMobil Refining & Supply Co.	Beaumont	348,500	55,410
Borger Refinery	ConocoPhillips/EnCana	Borger	146,000	23,200
Corpus Christi Complex	Flint Hills Resources	Corpus Christi	288,126	45,800
Corpus Christi Refinery	Citgo	Corpus Christi	156,000	24,800
Corpus Christi West Refinery	Valero Refining Co. Texas	Corpus Christi	142,000	22,600
Corpus Christi East Refinery	Valero Energy Corporation	Corpus Christi	115,000	18,300
Deer Park Refinery	Shell Deer Park Refining LTD	Deer Park	333,700	53,050
El Paso Refinery	Western Refining Company LP	El Paso	107,000	17,120
Houston Refinery	Lyondell Citgo Refining Co LTD	Houston	270,200	42,960
Houston Refinery	Valero Refining Co. Texas	Houston	83,000	13,200
Independent Refinery	Stratnor	Houston	100,000	16,000
McKee Refinery	Valero Energy Corporation	Sunray	158,327	25,170
Pasadena Refinery	Crown Central Petroleum Corp	Pasadena	100,000	16,000
Port Arthur Refinery	Total Petrochemicals Inc.	Port Arthur	233,500	37,120
Port Arthur Refinery	Motiva Enterprises LLC	Port Arthur	285,000	45,300
Port Arthur Refinery	Valero	Port Arthur	255,000	51,700
Penreco	Calumet	Houston	N/A	N/A
San Antonio Refinery	Age Refining Inc	San Antonio	10,308	1,640
Sweeny Refinery	ConocoPhillips/EnCana	Sweeney	229,000	36,400
Texas City Refinery	BP	Texas City	475,000	73,000
Texas City Refinery	Marathon Ashland Petroleum LLC	Texas City	72,000	11,400
Texas City Refinery	Valero Refining Co. Texas	Texas City	209,950	33,000
Three Rivers Refinery	Valero Energy Corporation	Three Rivers	90,000	14,000
Tyler Refinery	La Gloria Oil & Gas Co.	Tyler	55,000	8,700
TOTAL			**870,258**	**327,572**

Table 1- List of Refineries around Houston metropolitan area showing average crude distillation in barrels per day.

Road Type	NO_x [g/mi]	HC [g/mi]	CO [g/mi]	CO_2 [g/mi]	Fuel [Gal/mi]
Arterial	**2.4798**	0.5271	14.7475	**504.4681**	0.0597
Freeway	1.4813	0.2219	4.5354	276.3711	0.0840
Feeder	1.5626	0.1464	6.5745	296.5108	0.9775
Intersection	2.4155	0.3687	**14.8523**	478.3951	**1.7778**
All Roads	1.8530	**0.7710**	7.4959	355.4741	0.0466

Table 7- Original Summary Data of car emissions on Houston roads as reported by TSU DOTS HARC- Report (Yu & Qiao, 2004)

When U.S. Tier 2 Standards are Final (grams/mile)						
Vehicle fuels: Gasoline AND diesel		**Vehicle size: Up to 8,500 lbs. GVW**				
unless noted otherwise						**unless noted otherwise**
Useful life:		**120,000 miles**				
	Bins, category, size	**NMOG**	**CO**	**NOx**	**PM**	**HCHO**
U.S.	Bins					
emission	8	0.125	4.2	0.2	0.02	0.018
standards	7	0.090	4.2	0.15	0.02	0.018
	6	0.090	4.2	0.10	0.01	0.018
	5	0.090	4.2	0.07	0.01	0.018
	4	0.070	2.1	0.04	0.01	0.011
	3	0.055	2.1	0.03	0.01	0.011
	2	0.010	2.1	0.02	0.01	0.004
	1	0.000	0.0	0.00	0.00	0.000
	Average[a]	0.0663	2.8875	0.0763	0.0113	0.01225
California	Category	**(Diesel only)**				
LEV II	LEV[b]	0.090	4.2	0.07	0.01	0.018
emission	ULEV	0.055	2.1	0.07	0.01	0.011
standards	SULEV	0.010	1.0	0.02	0.01	0.004
	ZEV[c]	0.000	0.0	0.00	0.00	0.000

Acronyms Used on Table 12.13	
CO	Carbon Monoxide
GVW	Gross vehicle weight
HC	Hydrocarbons
HCHO	Formaldehyde
LDT	Light-duty truck
LEV	Low-emission vehicle
LVW	Loaded vehicle weight
MDPV	Medium-duty passenger vehicle (8,500-10,000 lbs. GVWR)
NMOG	Non-methane organic gases
NOx	Nitrogen oxides
PM	Particulate matter
SULEV	Super-ultra-low-emission vehicle
ULEV	Ultra-low-emission vehicle
ZEV	Zero-emission vehicle

Table 8- Original EPA exhaust emission standards for cars in effect in 2009 (cta/ornl.gov/data)

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