Spring 2012

Biofuel production and testing opportunities

Bernard William Newman
James Madison University

Recommended Citation

Newman, Bernard William, "Biofuel production and testing opportunities" (2012). *Senior Honors Projects, 2010-current*. 455.
https://commons.lib.jmu.edu/honors201019/455

Biofuel Production and Testing Opportunities

A Project Presented to

The Faculty of the Undergraduate

College of Science and Math

James Madison University

---

in Partial Fulfillment of the Requirements

for the Degree of Bachelor of Science

---

by Bernard William Newman

May 2012

Accepted by the faculty of the Department of Chemistry and Biochemistry, James Madison University, in partial fulfillment of the requirements for the Degree of Bachelor of Science.

FACULTY COMMITTEE:	HONORS PROGRAM APPROVAL:
Project Advisor: Chris Bachmann, Ph.D., Associate Professor, ISAT	Barry Falk, Ph.D., Director, Honors Program
Reader: Daniel M. Downey, Ph.D., Professor, Chemistry and Biochemistry	
Reader: Thomas C. DeVore, Ph.D., Professor, Chemistry and Biochemistry	
Reader: Richard Foust, Ph.D., Professor and Department Head, Chemistry and Biochemistry	

Dedication

This thesis is dedicated to my mother, father and sister, who have always encouraged me to do the very best I am capable of.

Table of Contents

List of Figures

Acknowledgements

First, I want to acknowledge and thank the professors on the Senior Honors Thesis Committee for their outstanding help and guidance. Specifically, I would like to express tremendous gratitude to Professors Foust, Falk and Bachmann for supporting my participation in an exciting cross-departmental research effort. Many deep thanks go to Professors Falk, Foust, Bachmann, Downey, Hughey, Amenta, Ralston, and DeVore, whose constant support and assistance was absolutely vital to the completion of this thesis.

I would also like to acknowledge the hard work of my research team at the College of Integrated Science & Technology, and to thank my advisor, Professor Reisner, for her support. Lastly, I would like to thank my family and friends who have supported me throughout this effort.

Abstract

Biofuels stand at the forefront of the United States' energy independence efforts and are the renewable fuels most likely to be used to bridge the growing gap between fossil fuel's cost effective availability and America's needs. With a known domestic commercial production capability, many economic, environmental, and geo-political benefits, and an ability to be used in our current transportation infrastructure biodiesel has emerged as the most credible near term alternative energy fuel.

The Senior Honors Project described herein in many ways has been an exercise in applied research. Although at first the project focused on the chemical evaluation of reactants and products involved in biodiesel production efforts, it eventually turned to applying the knowledge gained, by in depth review and those chemical evaluations, into concrete suggestions for protocols, procedures and inventions that might improve some of the nation's biodiesel production and testing effort.

To be widely accepted and commercially effective biodiesel must be processed to meet certain known standards published by the American Society for Testing and Materials [ASTM]. An ultimate goal of the research of this Honors Thesis is the establishment at James Madison University, and in accordance with ASTM standards, of an ability to efficiently utilize gas chromatography and specific analysis column to test for glycerin and other reactants in the production of biodiesel. A more immediate goal of the research is to create and demonstrate an ability to perform to ASTM standards the most pertinent of the required small batch biodiesel tests. The ability to improve the reactions involved in the ASTM testing methodology and/or the protocols and procedures acceptable to meet ASTM standards could have great impact on

biodiesel production in general and small batch bio-fuel operations such as James Madison University's [JMU] specifically.

After a thorough campus and laboratory inventory was performed, an equipment review was accomplished and a methodology agreement reached. Following an exhaustive literature and JMU project review the necessary laboratory equipment, chemicals, and reactants were identified and assembled. The equipment repair-laboratory assembly process is ongoing. Laboratory protocols and baselines were established and trial experiments were performed to help establish laboratory standards. Acceptable biodiesel samples were obtained and established experimental protocols are currently being performed in the hope of obtaining repeatable results.

New protocols and processes have been offered to test for biodiesel and an invention to improve the transesterfication reaction has been proposed. More specifically, the author has proposed the invention of a solid-state, heterogeneous catalyst, embedded onto a static mixer, to improve the necessary biodiesel transesterfication reaction, and not currently ASTM-approved biofuel production and quality testing procedures. A catalyst such as proposed, possibly working in even non-critical laboratory environments, could effectively and efficiently improve the biodiesel ASTM testing protocols.

I. Introduction

A. Overview of Energy and Transportation

Human beings have become dependent upon energy to help them perform work. In a broad sense energy could be defined as the potential that allows movement or the modification of any matter [including human].[1] Energy sources [e.g. oil, coal, bio-fuels] each have an energy content that can be expressed in energy per unit of volume or mass and it is only with the effective extraction of energy from each primary source that its use to perform work can be obtained.[2] Total world energy reserves are huge but are often not cost effective to exploit, for example solar and wind energy, or are not distributed near the location of need as is often the case for oil.[3] Historically, utility factors such as location, transferability, energy content, reliability, storability, flexibility, safety, price and cleanliness have frequently determined the choice of energy source.[4]

Machines have been used to perform work since the industrial revolution and with machines came energy and fuel demands.[5] At first factories to perform work were located near energy sources [e.g. waterfalls and coal mines] but with the development of engines, first steam [see Figure 1] and then combustion[6] and the ability to generate and distribute power in the form of electricity over great distances, location became more flexible. [7] The development and commercialization of the internal combustion engine, and particularly its use in transportation systems, made the efficient movement of people and goods possible, and this in turn led to the creation of our global trade network.[8] Continued industrial development and the use of combustion engines have also placed huge demands on fossil fuel.[9] Fossil fuel is a general term used to describe buried combustible geologic deposits of organic materials that are formed by the death and decay of plants and animals and that have been converted to coal, crude oil, heavy oils, or natural gas, by exposure to heat and pressure in the earth's crust over hundreds of millions of years. Fossil fuels today account for almost 90% of the United States' total energy consumption and for over 98% of the United States' transportation energy use.[10]

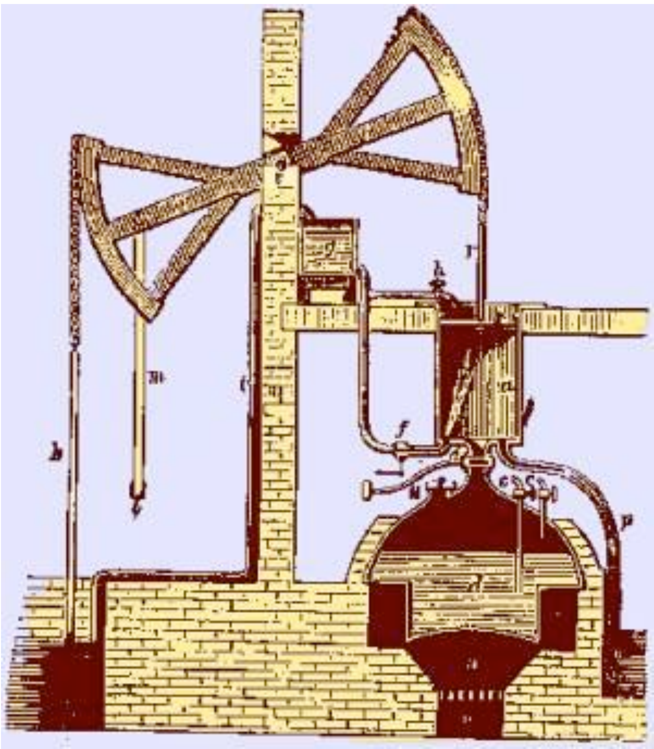
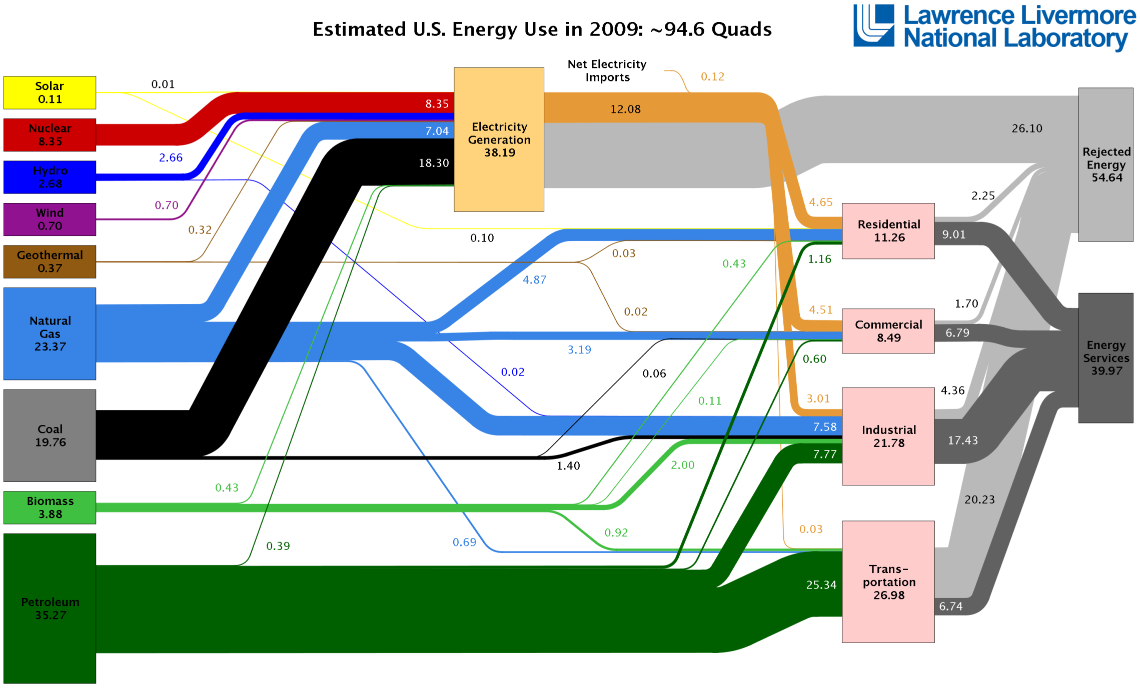


Figure 1. 1712 Illustration of Thomas Newcomen's Steam Engine

In 1712, Thomas Newcomen together with John Calley built their first steam engine on top of a water filled mineshaft and used it to pump water out of the mine. The Newcomen steam engine was the predecessor to the Watt steam engine and it was one of the most interesting pieces of technology developed during the 1700's. The invention of engines, the first being steam engines, was very important to the industrial revolution

The scope of human activity and the level of a nation's economic development are well correlated to its energy consumption.[11] The more energy used, the greater the amount of work realized, and the more a society can advance. Work related to human activity can broadly be thought of in terms of modifying of the environment (for example making space suitable for human activity), appropriating resources (for example agricultural or mineral collection and waste disposal), resource processing (for example of biomass, materials or produced goods), and transfer (for example of freight, people, and information).[12]

Transportation on land, sea and air, made possible by the internal combustion engine, notably gas turbines and diesel engines, has accounted for an ever increasing share of total energy demand and in advanced countries now accounts for between 20 and 25% of total energy use[13]. Transportation accounted for about 27% of total energy demand in the United States in 2009 (see Figure 2).[14]



Source: LLNL 2010. Data is based on DOE/EIA-0384(2009), August 2010. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Figure 2. Estimated U.S. Energy Use in 2009

Transportation accounted for approximately 27% of U.S. energy use in 2009

Transportation worldwide is almost completely dependent upon petroleum-derived fuels [>90%][15] and the growth in world oil and petroleum demand has been almost completely a result of growth in the demand for transportation.[16] Since 2004 transportation has accounted for more than 70% of U.S. petroleum use (see Figure 3).[17]

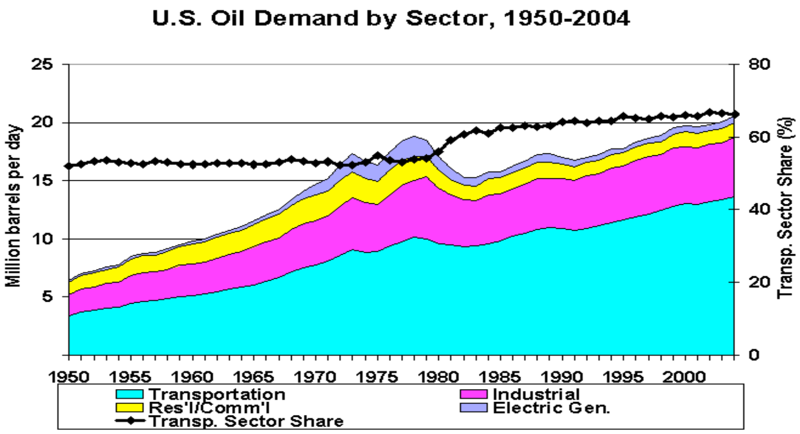


Figure 3. Annual Energy Review: U.S. Energy Demand

By 2004, more than 70% of all oil used in the U.S. is used for transportation.

In 2006, the overwhelming bulk of US petroleum consumption was for motor gasoline and other vehicle fuels (see Figure 4).

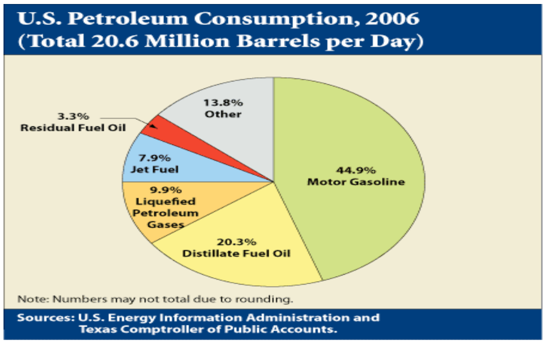


Figure 4. U.S. Petroleum Consumption in 2006

By 2006 vehicle fuels dominated U.S. petroleum use.

B. Fossil Fules

1. Transportation

Petroleum derived fuels came to dominate the transportation sector as a result of their low cost, ease of storability, transportability, and the efficiency of their use in internal combustion engine vehicles.[18] The U.S. was for many years self-sufficient in oil, but began importing more oil than it produced in 1994 (see Figure 5). By 2008, 57 percent [57%] of the oil consumed in the U.S. was imported from foreign countries (see Figure 6). The top five source nations for net petroleum and petroleum product imports to the U.S. in 2008 were Canada, Saudi Arabia, Mexico, Venezuela, and Nigeria.[19]

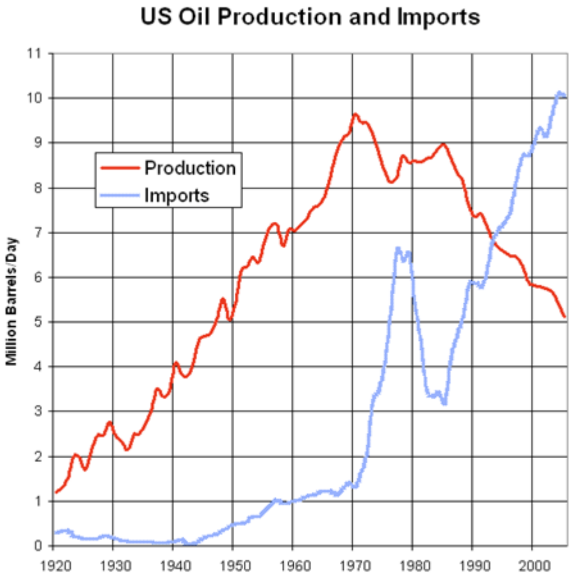
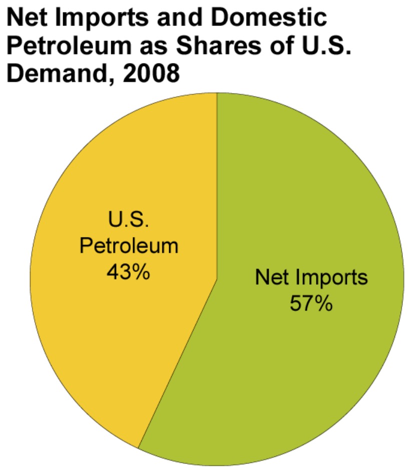


Figure 5. U.S. Oil Production and Imports

By 1994 the U.S. imported more oil than it produced.



Source: Energy Information Administration.

Figure 6. Net Imports and Domestic Petroleum as Shares of U.S. Demand

By 2008 the U.S. imported almost 60% of its petroleum.

With a rising world population and increasing demand from China and other developing nations, current producers may not have the ability to produce, from proven reserves and on a daily basis, the increasing oil that the world almost certainly will require.[20] Also, there are geological limits to the output capabilities of current oil production fields, and even if new ones are found to add to, or replace, the current ones this may not be done in a timely or economical manner.[21]

A great amount of current oil reserves are located in unstable areas of the world including the Middle East, Nigeria, Venezuela and Russia,[22] and it is by no means certain that they will be available in times of conflict or competition. As the U.S. Department of Defense as a whole, and the United States Navy specifically, are the two largest users of energy on earth [23] the unfavorable location of much of the world's oil could compromise them going forward.

The United States uses far more petroleum than any other country and its' dependence on oil based fuels continues to increase (see Figure 7).[24]

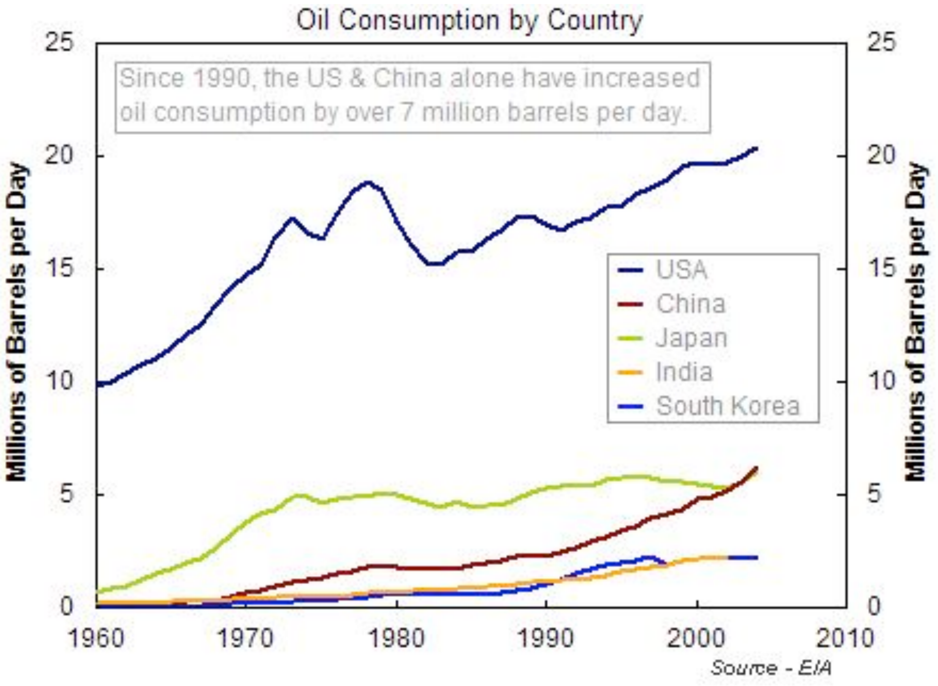


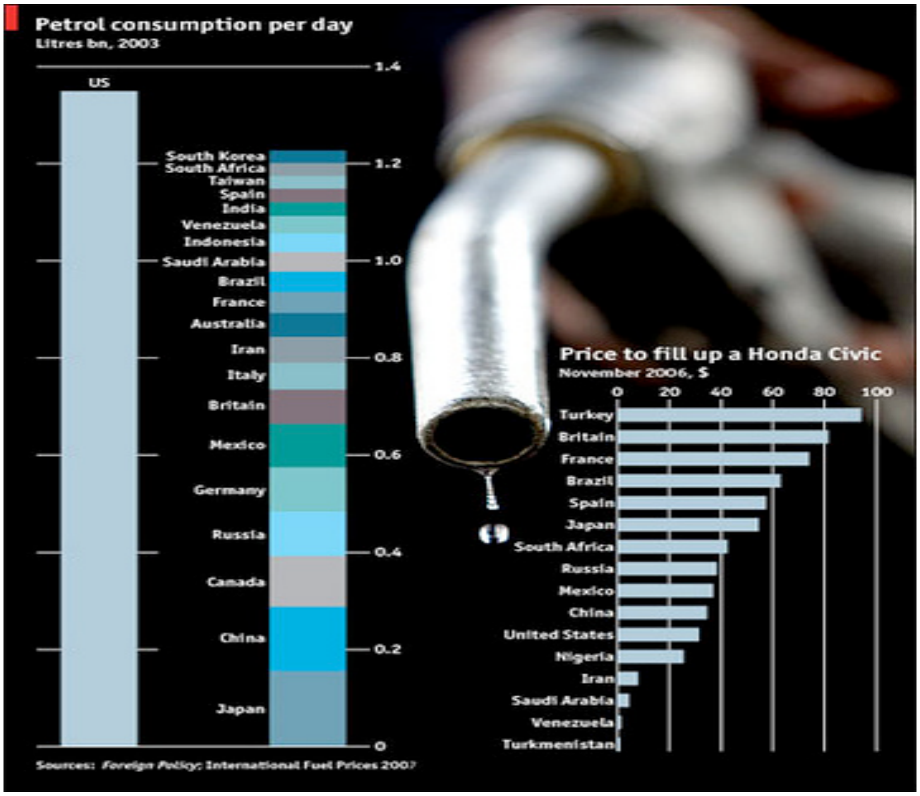
Figure 7. Oil Consumption By Country

U.S. and China petroleum use dwarfs all other countries.

The world's oil reserves are huge if not always easily accessible and it is important to note that even with the rapid growth of global demand for petroleum products, it is estimated that less than half the world's total conventional oil reserves will have been actually exhausted by 2025.[25] This estimate includes existing oil reserves and anticipated reserves resulting from new technologies and discoveries, but it is a fact nonetheless that the world's oil reserves have steadily increased even as consumption has also been rising.[26]

Given this reserve/consumption track record, and that as technology advances net proven recoverable reserves and production will also likely increase, and recognizing that the history of oil production is filled with cycles of surplus and shortage [27] it is impossible to say exactly how long conventional non-renewable fossil fuels will continue to be the primary energy source for the world's transportation needs. However, the gap between supply and demand has been steadily narrowing and it is possible that global and U.S. production from acceptable, proven, conventional sources has “peaked.” [28] It is the gap that may create the world’s main energy issues going forward.[29]

Restating, the U.S. far exceeds any other country in oil consumption and currently consumes 25% of the amount of oil that the world as a whole is consuming. The U.S. consumes more oil than its two closest competitors, Japan and China, and it continues to grow its oil consumption. The graph in Figure 8 demonstrates this enormous oil consumption as it occurred in 2004.


Petrol consumption per day
Litres bn, 2003

Price to fill up a Honda Civic
November 2006, $

Sources: Foreign Policy; International Fuel Prices 2007

Figure 8. Petroleum Consumption Per Day

In 2004, the U.S. consumed more oil than the next 20 oil-consuming countries combined.

By 2004 the U.S. consumed more petroleum per day than the next 20 oil-consuming countries combined, and while the data has changed somewhat since 2004 and now would reflect the recent rapid growth of China and India, the issue of extremely high per/day U.S. oil consumption remains.[30]

With a highly mobile society, enormous dependence on imported oil, and an advanced petroleum based transport system the United States has been and is extremely vulnerable to energy disruption.[31] As we can see in Figure 9, past oil import disruption and past rapid oil price escalation has had known negative economic effect on the United States' economy as measured by its Gross Domestic Product [GDP]. GDP refers to the market value of all officially recognized final goods and services produced within a country in a given period and GDP per capita is often considered an indicator of a country's standard of living.[32]

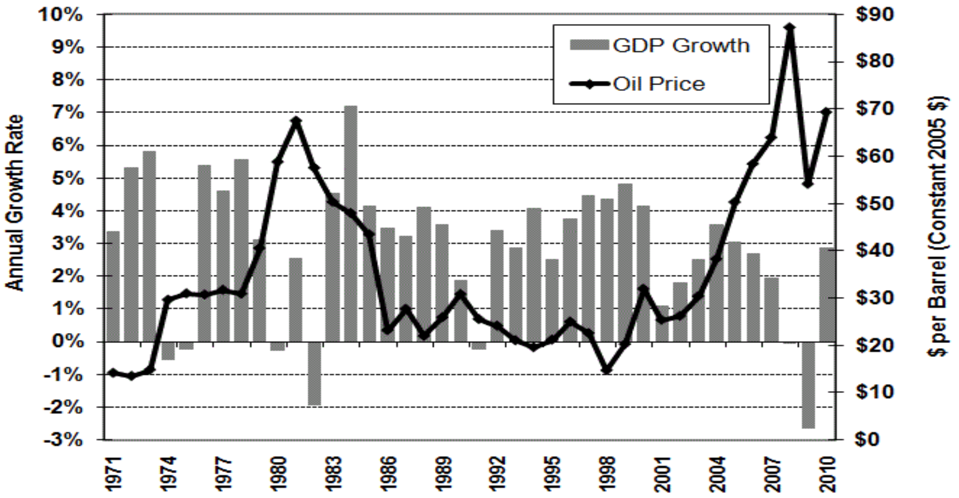


Figure 9. Annual Growth Rate and Oil Price

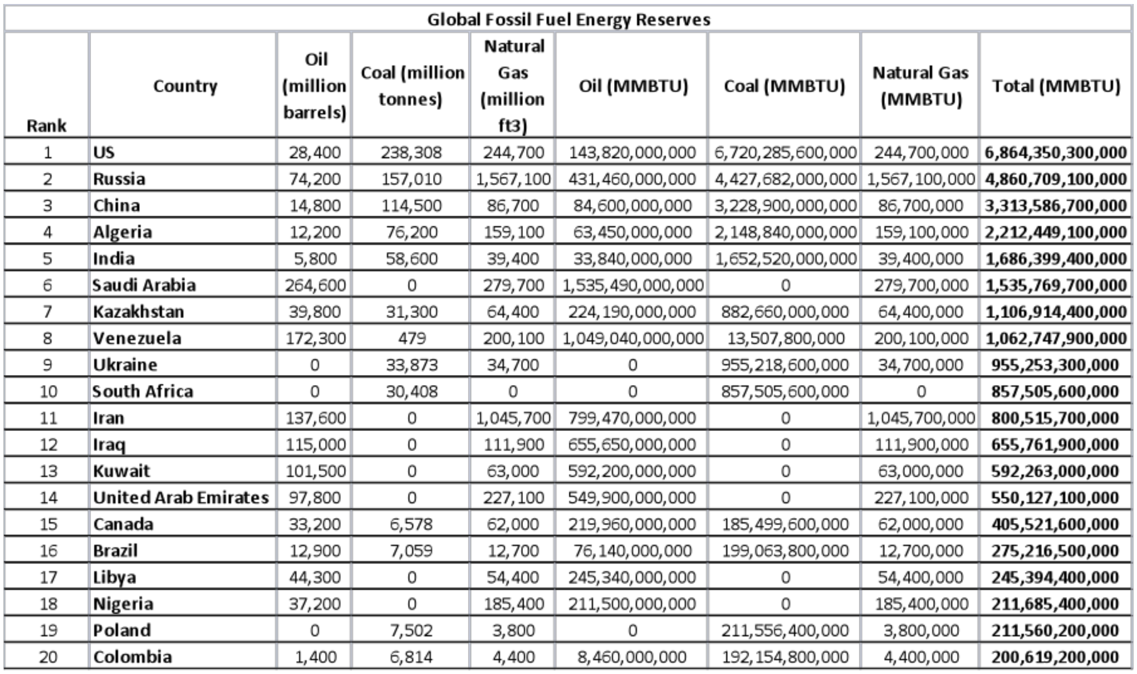
In its Transportation Energy Book of 2011, the Department of Energy indicated that major oil price shocks have disrupted world energy markets five times in the past 30 years (1973-74, 1979-80, 1990-91, 1999-2000, 2008). An economic recession in the U.S. followed most of these "price shocks."

With the world's current transportation systems now more than 90% dependent on global fossil oil reserves, and those same oil reserves currently vital to supplying much of the world's other energy needs,[33] the production and distribution of virtually all goods on earth is at this time highly dependent on global fossil oil reserves. Although there is conflicting data,[34] credible studies indicate that with sustained consumption,[35] at some [likely soon] point in time, these fossil oil reserves will become depleted or in some way insufficient to meet desired world energy needs.[36] If and when that point does arrive, the global economy will be altered forever and there will be profound effects in the United States.[37] Competition and conflict for energy resources have routinely occurred in the past and are likely to occur in the future.[38] As the United States currently is more dependent on liquid fossil fuel energy than any other nation in the world[39], it is imperative that it has a strategy to effectively manage the almost inevitable coming disruption to its energy supply and crucial transportation systems. The rapid development of the biodiesel industry may be such a strategy.

2. Reserves and Consumption

To further understand the global energy situation one must consider multiple complex issues and be willing to recognize that the statistical, environmental, geo-political, security, and scientific "facts" that could help to solidify an understanding of "energy" matters, are more or less constantly in flux.[40]

A key energy concept that needs to be understood is the ever-changing relationship between various fossil energy reserves and fossil energy consumption. While the United States has more total proven **fossil fuel** [i.e. coal, natural gas, oil] energy reserves, as calculated in MMBTUs, than any other country in the world, approximately sixty-five percent [65%] of the world's proven **oil** reserves are concentrated in the Middle East (see Figure 10).[41]



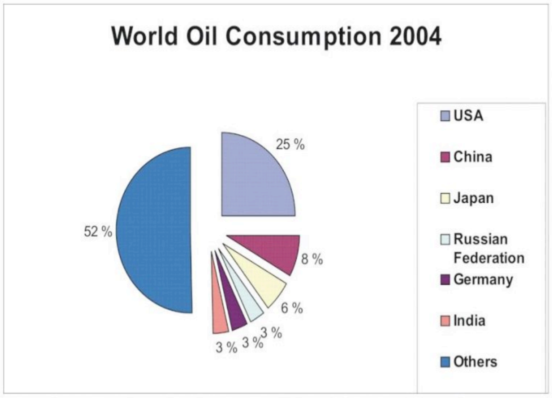
Global Fossil Fuel Energy Reserves

Rank	Country	Oil (million barrels)	Coal (million tonnes)	Natural Gas (million ft3)	Oil (MMBTU)	Coal (MMBTU)	Natural Gas (MMBTU)	Total (MMBTU)
1	**US**	28,400	238,308	244,700	143,820,000,000	6,720,285,600,000	244,700,000	**6,864,350,300,000**
2	**Russia**	74,200	157,010	1,567,100	431,460,000,000	4,427,682,000,000	1,567,100,000	**4,860,709,100,000**
3	**China**	14,800	114,500	86,700	84,600,000,000	3,228,900,000,000	86,700,000	**3,313,586,700,000**
4	**Algeria**	12,200	76,200	159,100	63,450,000,000	2,148,840,000,000	159,100,000	**2,212,449,100,000**
5	**India**	5,800	58,600	39,400	33,840,000,000	1,652,520,000,000	39,400,000	**1,686,399,400,000**
6	**Saudi Arabia**	264,600	0	279,700	1,535,490,000,000	0	279,700,000	**1,535,769,700,000**
7	**Kazakhstan**	39,800	31,300	64,400	224,190,000,000	882,660,000,000	64,400,000	**1,106,914,400,000**
8	**Venezuela**	172,300	479	200,100	1,049,040,000,000	13,507,800,000	200,100,000	**1,062,747,900,000**
9	**Ukraine**	0	33,873	34,700	0	955,218,600,000	34,700,000	**955,253,300,000**
10	**South Africa**	0	30,408	0	0	857,505,600,000	0	**857,505,600,000**
11	**Iran**	137,600	0	1,045,700	799,470,000,000	0	1,045,700,000	**800,515,700,000**
12	**Iraq**	115,000	0	111,900	655,650,000,000	0	111,900,000	**655,761,900,000**
13	**Kuwait**	101,500	0	63,000	592,200,000,000	0	63,000,000	**592,263,000,000**
14	**United Arab Emirates**	97,800	0	227,100	549,900,000,000	0	227,100,000	**550,127,100,000**
15	**Canada**	33,200	6,578	62,000	219,960,000,000	185,499,600,000	62,000,000	**405,521,600,000**
16	**Brazil**	12,900	7,059	12,700	76,140,000,000	199,063,800,000	12,700,000	**275,216,500,000**
17	**Libya**	44,300	0	54,400	245,340,000,000	0	54,400,000	**245,394,400,000**
18	**Nigeria**	37,200	0	185,400	211,500,000,000	0	185,400,000	**211,685,400,000**
19	**Poland**	0	7,502	3,800	0	211,556,400,000	3,800,000	**211,560,200,000**
20	**Colombia**	1,400	6,814	4,400	8,460,000,000	192,154,800,000	4,400,000	**200,619,200,000**

Figure 10. Global Fossil Fuel Energy Reserves

As calculated form BPs 2010 Review of Global Fossil Energy the United States has more known and recoverable fossil fuel reserves than any other nation.

It is from fossil oil reserves that the world's petroleum is produced. In 2010, despite using much more, the U.S. was responsible for 9.1% of the world's petroleum production and 7.5% of the world's crude oil production.[42] The United States has for many years consumed much more oil than it has produced and by 2004 it consumed over 50% of the worlds' oil, as demonstrated in Figure 11.

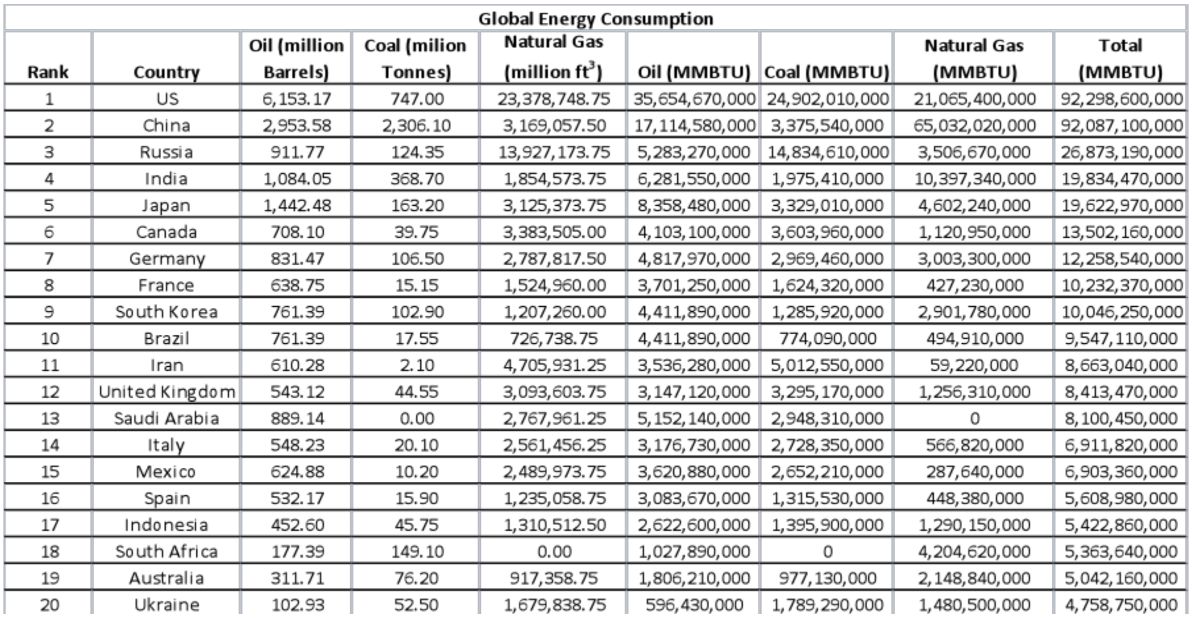


Source: "Statistical Review of World Energy 2005",BP.

Figure 11. World Oil Consumption in 2004

For many years, the U.S. consumed about one half of the worlds' oil production.

While the United States likely still consumes more total energy, as calculated in MMBTUs, than any other nation, China's energy use has rapidly increased and by the time of this reading it might well have surpassed the United States. [43] The two nations, in any case, consume most of the worlds' energy production (see Figure 12).



Global Energy Consumption

Rank	Country	Oil (million Barrels)	Coal (milion Tonnes)	Natural Gas (million ft^3)	Oil (MMBTU)	Coal (MMBTU)	Natural Gas (MMBTU)	Total (MMBTU)
1	US	6,153.17	747.00	23,378,748.75	35,654,670,000	24,902,010,000	21,065,400,000	92,298,600,000
2	China	2,953.58	2,306.10	3,169,057.50	17,114,580,000	3,375,540,000	65,032,020,000	92,087,100,000
3	Russia	911.77	124.35	13,927,173.75	5,283,270,000	14,834,610,000	3,506,670,000	26,873,190,000
4	India	1,084.05	368.70	1,854,573.75	6,281,550,000	1,975,410,000	10,397,340,000	19,834,470,000
5	Japan	1,442.48	163.20	3,125,373.75	8,358,480,000	3,329,010,000	4,602,240,000	19,622,970,000
6	Canada	708.10	39.75	3,383,505.00	4,103,100,000	3,603,960,000	1,120,950,000	13,502,160,000
7	Germany	831.47	106.50	2,787,817.50	4,817,970,000	2,969,460,000	3,003,300,000	12,258,540,000
8	France	638.75	15.15	1,524,960.00	3,701,250,000	1,624,320,000	427,230,000	10,232,370,000
9	South Korea	761.39	102.90	1,207,260.00	4,411,890,000	1,285,920,000	2,901,780,000	10,046,250,000
10	Brazil	761.39	17.55	726,738.75	4,411,890,000	774,090,000	494,910,000	9,547,110,000
11	Iran	610.28	2.10	4,705,931.25	3,536,280,000	5,012,550,000	59,220,000	8,663,040,000
12	United Kingdom	543.12	44.55	3,093,603.75	3,147,120,000	3,295,170,000	1,256,310,000	8,413,470,000
13	Saudi Arabia	889.14	0.00	2,767,961.25	5,152,140,000	2,948,310,000	0	8,100,450,000
14	Italy	548.23	20.10	2,561,456.25	3,176,730,000	2,728,350,000	566,820,000	6,911,820,000
15	Mexico	624.88	10.20	2,489,973.75	3,620,880,000	2,652,210,000	287,640,000	6,903,360,000
16	Spain	532.17	15.90	1,235,058.75	3,083,670,000	1,315,530,000	448,380,000	5,608,980,000
17	Indonesia	452.60	45.75	1,310,512.50	2,622,600,000	1,395,900,000	1,290,150,000	5,422,860,000
18	South Africa	177.39	149.10	0.00	1,027,890,000	0	4,204,620,000	5,363,640,000
19	Australia	311.71	76.20	917,358.75	1,806,210,000	977,130,000	2,148,840,000	5,042,160,000
20	Ukraine	102.93	52.50	1,679,838.75	596,430,000	1,789,290,000	1,480,500,000	4,758,750,000

Figure 12. Global Energy Consumption in 2010

The U.S. and China far surpass all other nations in fossil fuel consumption.

Energy use per capita correlates well with human economic activity and, as we can see in Figure 13, only Canada and Saudi Arabia consume more energy than does the United States on a per capita basis.[44].

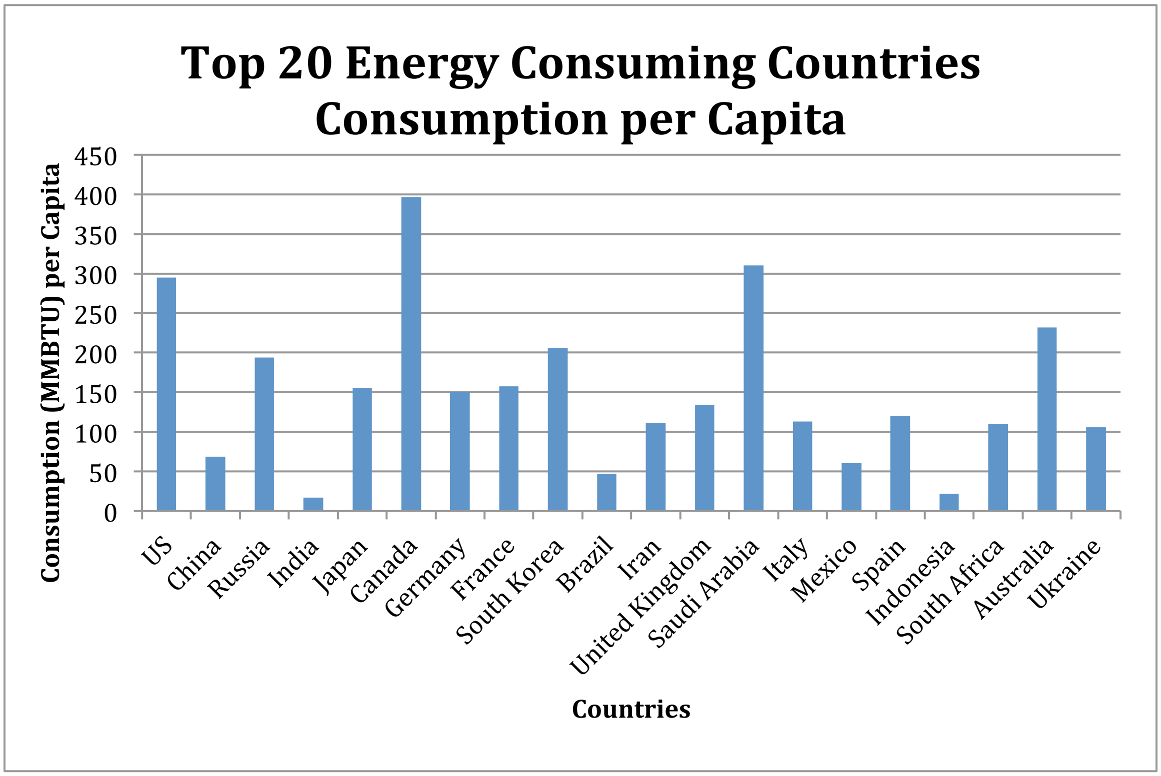
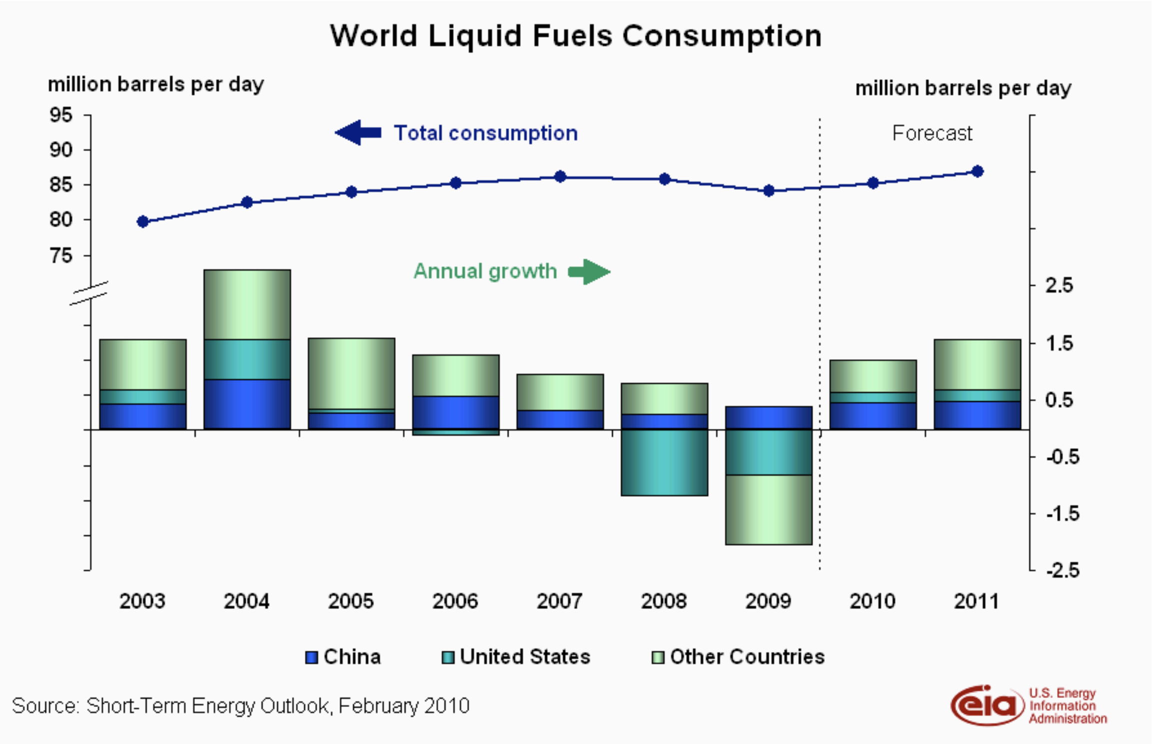


Figure 13. Top 20 Energy Consuming Countries: Consumption per Capita

Energy Per Capita can be used to measure human economic activity

Estimates of current proven reserves [i.e. supply] and consumption [i.e. demand] are constantly being revised as new data is collected for analysis. The rise in energy consumption and therefore demand by China and other countries, principally India, can be seen by comparing data such as British Petroleum's in Figure 12 to earlier similar information.[45] The rise can also be measured by monitoring the world's liquid fuel consumption,[46] as demonstrated by the graph in Figure 14.



Source: Short-Term Energy Outlook, February 2010

Figure 14. World Liquid Fuels Consumption

Liquid fuel use is a way to demonstrate a rise in fossil fuel demand, energy consumption, and economic growth

The CIA's 2009 Ranking Table of proven oil reserves[47] has agreed with that of BP's for more than a decade and documents that the United States has not been in domestic control of its oil needs a considerable period of time (see Figure 15).

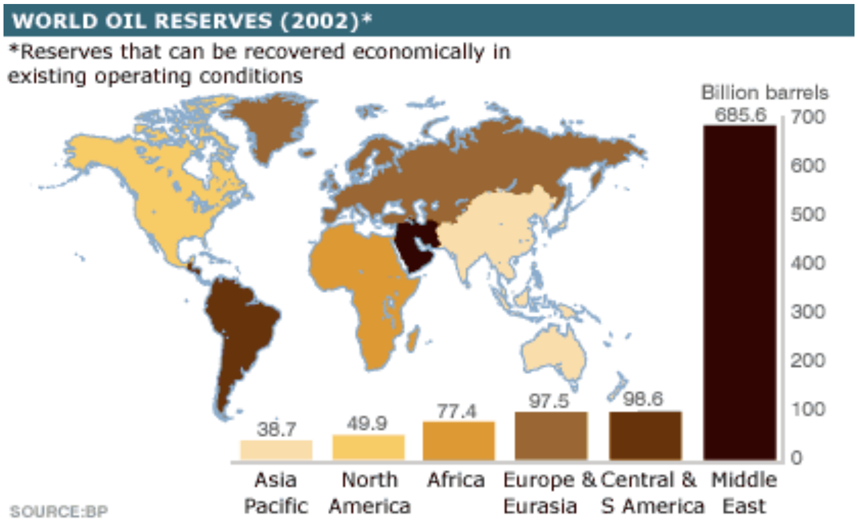
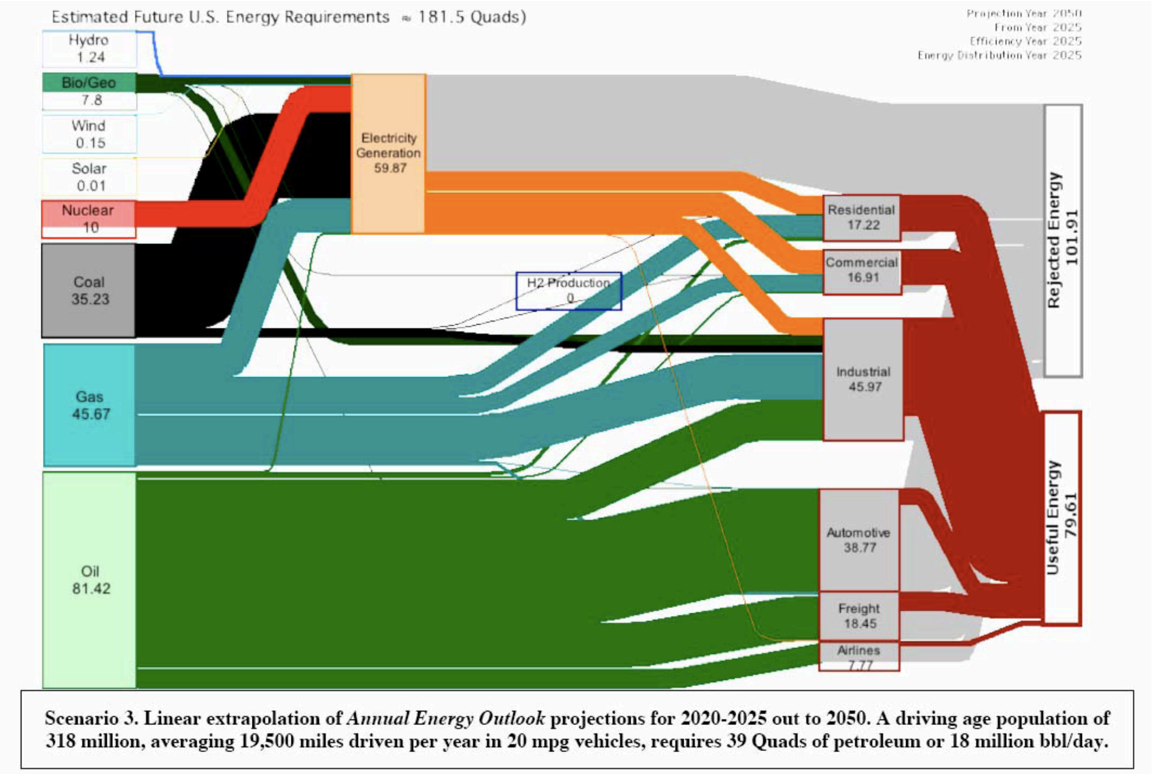


Figure 15. Proven World Oil Reserve

World oil reserves a decade ago (2002) help document the prolonged U.S. dependence on foreign sourced oil.

Given the importance of oil derived fuel to U.S. and world transportation systems and the distinct possibility that global oil reserves will at some point rapidly deplete or become unavailable,[49] Lawrence Livermore National Laboratory compiled a detailed view of United States energy consumption from numerous data sources as well as a predictive model. The graphs generated from this data, as seen in Figures 2 and 16 demonstrate that the United States' energy needs are predicted to approximately double between now and 2050 while its' dependence on liquid fuels is not expected to appreciably diminish.



Scenario 3. Linear extrapolation of *Annual Energy Outlook* projections for 2020-2025 out to 2050. A driving age population of 318 million, averaging 19,500 miles driven per year in 20 mpg vehicles, requires 39 Quads of petroleum or 18 million bbl/day.

Figure 16. Estimated U.S. Energy Use in 2050.

United States energy needs are expected to double by 2050, but we are expected to still be dependent on liquid transportation fuels at that date.

To summarize fossil fuel supply and demand, the current United States oil situation simply seems unsustainable;[51] barring major technological and environmental advances, "Peak Oil" production in the United States has possibly already occurred; while America has large amounts of proven reserves[R],[52] and increasing production capabilities [P],[53] a thorough review of our Reserve/Production ratio [R/P] illustrates not only how quickly we can use up our own oil, but also how dependent the ratio is on oil imports; the United States is no longer in control of its energy needs; world fuel consumption which has shifted over the years, has been changing even more rapidly recently; there is now a very tight market for oil globally and even a small change in oil supply can have dramatic marketplace effects; the security implications of a rapid depletion of the world oil supply becomes even more clear when one considers history; and that the United States military is the world's largest consumer of liquid fuel [currently overwhelmingly produced from fossil fuel sources].[54] The United States currently uses petroleum more than any other fuel for energy and at least 2/3 of this petroleum is used in transportation. Also, in 2008 this amounted to 37% of the total energy we consumed on a daily basis or about 19.5 million barrels/day and that today we consume even more oil. Sadly, net imports and domestic petroleum as shares of United States data demand show that the United States' dependence on Middle Eastern oil has actually increased since the 1973 Arab oil embargo when we were importing only 35% of our oil. In fact looking at US oil production and imports over the past 90 years one can see that US production may well have peaked around 1970 and that by 2008 the United States was importing some 65% of the oil needed for refined products.[55]

3. Emerging Fossil Fuels

Besides the known and proven world fossil oil reserves available to meet the world's transportation need, there are also a number of so-called "unproven" or "emerging" fossil energy reserves that might be usable. Those with potentially large enough reserves to fill the enormous need that will be created should current oil supplies rapidly become unavailable include coal, natural gas, "heavy" oil, tar sand oils, oil shale, and even methane hydrates. Each of these has its own environmental and social challenges to overcome and none is yet compatible with the existing transportation infrastructure.[56]

4. Pollution

Unfortunately, with combustion comes pollution. Pollutants that are created and must be dealt with include carbon dioxide (CO_2) produced (along with water) when combusting a carbon fuel, carbon monoxide (CO) produced by incomplete combustion (not enough oxygen or low temperature), oxides of nitrogen (NO_X) produced in internal combustion engines by heat and pressure, , oxides of sulfur (SO_X) as all fossil fuels, in particular diesel and coal, contain sulfur, hydrocarbons (HC) or volatile organic compounds (VOCs) in unburned petroleum due to an incomplete burn, and particulate matter (PM) usually particulate carbon released from the fuels and greatly in diesel combustion.[57]

C. Biofules

1. Background and policy

The development of domestically produced, clean, renewable fuel has been a stated strategic policy goal of the United States for a great many years and was codified in 2005 with the passage of the 2005 Energy Policy Act.[58] In addition to the obvious economic merits for this policy there were also a number of security and environmental concerns that were drivers.[59]

Understanding the many characteristics of fossil oil depletion as well as the impact the depletion will inevitably have on transportation systems, and therefore the standard of living within the United States, has been a primary concern for this investigator, as well as the development of a credible replacement for those fossil fuels.

Biofuels as compared to fossil fuels are renewable, efficient and relatively clean burning. Biofuels can at this time be divided into two main product lines, those that blend with or replace gasoline, and those that blend with or replace middle distillate fuels such as diesel fuel or home heating oil .The dominant gasoline replacement today is ethanol and the dominant middle distillate replacement is biodiesel.[60]

Renewable biofuels that are compatible with our current transportation infrastructure and that can be gradually introduced into our oil-based economy are the ones most likely to be produced and to actually help with the United States' necessary transition to a clean energy society. The two most promising renewable near term solutions to the impending fossil oil crisis are ethanol and biodiesel. [61]As biodiesel and ethanol can be used in existing vehicles and can be disbursed through the already existing fuel distribution infrastructure [62] they have huge advantages over other renewable fuels such as wind, water, gaseous fuels [i.e. hydrogen] and electricity.[63] Biodiesel and ethanol also offer potentially beneficial pollution/environmental impacts [gas vs. ethanol/ biodiesel vs. diesel] and can be produced domestically[64].

Biofuels are in actuality not a particularly "new" kind of fuel. In fact, biofuels were utilized well prior to the use of petroleum-based fuels. Ethanol derived from corn was used to power many early automobiles including Henry Ford's Model-T[65] and, the first diesel engine, created by Rudolf Diesel in Germany, was actually powered by peanut oil.[66]

2. Biomass

The first fuel ever used was probably what we now call "biomass." Biomass can be defined as renewable, organic, non-fossil material including all plants and animals, and their byproducts [such as wood, oil, droppings and fat].[67] When biomass is ignited and used as a fuel to create light, heat, electricity, or combustion within an engine, it becomes a biofuel. Wood, used in a prehistoric fire, was therefore probably both the first fuel and biofuel. Biofuels have changed very little over the course of earth's history with each biofuel used today containing approximately the same BTUs per pound as similar ones did millions of years ago.[68]

3. Fuels and Engines

The most significant gains and efficiencies on the energy front have in actuality been accomplished by advances in engines and pistons rather than by the discovery of new or unique fuel sources. Historically, the development of engines and the evolution of fuels have gone hand in hand.[69] Fuels, including biofuels, can be differentiated by their ability to be utilized in either “spark-ignition” engines or in “compression” engines. Ethanol, for example, is a very good spark ignition biofuel and biodiesel, for example, an equally good compression biofuel. The differences between how the two engine types function lead to their fuels’ having quite different characteristics as well.[70] Diesel high compression engines are much more energy efficient than their gasoline spark ignition counterparts and therefore have typically been the engine of choice when an application has required heavy power use. Trains, trucks, farm and construction equipment for example is usually powered by diesel engines. [71]

4. Debates

The recent race to replace fossil fuels with renewable biofuels has sparked several debates. One debate concerns the so-called “Energy Input vs. the Energy Output” equation of biofuels. Many people falsely believe that more energy is required to make ethanol and biodiesel than one ultimately derives from them when they are utilized; and, although numerous studies have demonstrated that this is not true, the debate continues.[72] The second large debate generated by biofuel development could be called “The Great Fuel vs. Food Debate” in which virtually every aspect of different priorities for land utilization strategies are heard.[73] In fact there is little for Americans to debate in this matter as for them it is not really an “either /or” choice; the vast land rich United States can grow plants for both food and fuel.[74]

5. Algae

Although the use of algae as a biofuel substrate has just recently been made newsworthy, JMU has been investigating this possibility for years. The use of algae, rather than land-based crops, could eliminate the ongoing fuel vs. food debate and allow many land poor nations to become energy rich. The necessary harvesting, commercial processes and infrastructures for algae to bring cost effective benefit have not yet developed but some interesting progress has been made.[75]

D. Biodiesel

1. Background and Overview

Biodiesel is safe and can be used in most diesel engines with little or no modification. Although biodiesel can be used in its pure form, it is usually blended with standard diesel fuel. Blends are indicated by the abbreviation Bxx, where xx is the percentage of biodiesel in the mixture. For example, the most common blend is B20, or 20 percent biodiesel to 80 percent standard; B100 refers to pure biodiesel. Biodiesel is not a catchall term. There is also a formal, technical definition that is recognized by the American Society for Testing and Materials, the organization responsible for providing industry standards. According to the National Biodiesel Board [NBB] the technical definition of biodiesel is: A fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D6751. [76] ASTM D6751-11 is the specification that covers biodiesel fuel blend stock, B100, in Grades S15 and S500 for use as a blend component with middle distillate fuels. This specification prescribes the required properties of diesel fuels at the time and place of delivery. The requirements stated may also be applied at other points in the production and distribution system. The standard states that the biodiesel specified shall be mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats and shall undergo chemical analysis for flash point, methanol, water and sediment, kinematic viscosity, sulfated ash, oxidation stability, sulfur, copper strip corrosion, octane number, cloud point, acid number, carbon residue, total and free glycerin, phosphorus, reduce pressure distillation temperature, atmospheric equivalent temperature, combined calcium and magnesium, and combined sodium and magnesium. The Scope of the ASTM Standard as well as the detailed protocol and tests included within the ASTM Biodiesel Standard are available to the public.

Diesel engines and gasoline engines are quite similar. They are both internal combustion engines designed to convert the chemical energy available in fuel into mechanical energy. In automobiles this mechanical energy moves pistons up and down inside cylinders. The pistons are connected to a crankshaft, and the up-and-down motion of the pistons, known as linear motion, creates the rotary motion needed to turn the wheels of a car forward.[77]

Both diesel engines and gasoline engines convert fuel into energy through a series of small explosions [or combustions]. The major difference between diesel and gasoline engines is the way these explosions happen. In a gasoline engine, fuel is mixed with air, compressed by pistons and ignited by sparks from spark plugs. In a diesel engine, however, the air is compressed first, and then the fuel is injected. Because air heats up when it's compressed, the fuel ignites. A diesel engine uses a four-stroke combustion cycle just like most gasoline engines. The four strokes are an intake stroke in which the intake valve opens up, letting in air and moving the piston down, a compression stroke during which the piston moves back up and compresses the air, a combustion stroke in which as the piston reaches the top, fuel is injected at just the right moment and ignited, forcing the piston back down, and an exhaust stroke where the piston moves back to the top, pushing out the exhaust created from the combustion out of the exhaust valve. The diesel engine has no spark plug. It intakes air and compresses it, and then injects the fuel directly into the combustion chamber [direct injection]. The heat of the compressed air lights the fuel in diesel engines.[78]

While biodiesel fuel can be used in any diesel engine vehicle, including passenger cars, heavy-duty trucks and farm equipment, without making any modifications to the engine, its use must be done with care. The most challenging issue with bio-diesel as a fuel source is the quality of the fuel itself. While fuel standards for biodiesel have now been created, they are not nearly as stringent as those the United States has for gasoline and even for petroleum diesel. The lack of consistent quality among all producers is an issue that has everyone - the biodiesel industry, automakers, engine suppliers, consumers and this investigator concerned.[79] It is also a major driver of the research done for this senior thesis.

There are several issues of special note that must be dealt with in bio diesel fuel[80] with the two most important of these being temperature control and clogging. Because biodiesel fuel is made with vegetable-based products, the temperature it is stored at is more critical than with petroleum diesel. As a result, fueling stations need to treat biodiesel a bit differently than other fuels. If it sits in a warm storage tank for too long, it can grow mold, and if it is stored at too cold a temperature, it will thicken and become difficult to dispense. These problems typically occur if the biodiesel is not used quickly enough. Owners using biodiesel should also watch for signs that fuel filters and systems are clogging, particularly when biodiesel is first used. Biodiesel acts as a lubricant, which means that it can loosen deposits that are stuck in fuel lines and in the fuel tank, which in turn could clog fuel filters, injectors, or other parts of the fuel system.[81]

Since these issues relate only to pure biodiesel fuel, not blends, the risks of using biodiesel are significantly less, some even say insignificant, with low biodiesel blends.[82] Today, most passenger diesel vehicles will remain covered by the manufacturer's warranty if an owner is using B5 biodiesel. As biodiesel production standards increase, manufacturers have indicated they may warranty vehicles that use up to B20 biodiesel. Where opinions deviate greatly is with biodiesel blends that use more than 20 percent or with pure biodiesel. Many manufacturers feel that even B100 that has been produced by a reputable manufacturer should not be used in a vehicle engine as it would likely result in engine damage. Others feel that it may be possible to use B100, without any adverse effects, so long as the quality standards are high.

Biodiesel is simply a biofuel that can be used as an alternative to diesel fuel and that is made from renewable biological sources[83]. Sources are varied and can include many types of grown products such as nuts, soybeans, peanuts, corn, seeds and many vegetables, a variety of animals that have animal fats and possibly even algae[84]. Biodiesel production has attracted a great amount of attention since the 1980's due to its supposedly many environmental and economic benefits.[85]

The idea behind using biodiesel rather than fossil sources as a fuel, that is using plant oils and the like rather than petroleum products, has a remarkably long history. E. Duffy and J. Patrick, in 1893, were among the first to postulate the idea of using biological fuels[86] and, as stated earlier, in that same year, Rudolf Diesel, mentioned earlier, conducted the first test of an engine to run on a plant oil based fuel[87]. Diesel actually tested a variety of vegetable oils as potential fuel for the engine that now has his name[88]. Diesel went on to demonstrate his engine working on peanut oil in at the International Exhibition of 1900. Interestingly, Diesel in 1912 speaking at the Great Britain Technological Institute stated: "…usage of plant oils as fuel for cars may seem insignificant nowadays but such oils, with time may become as important as coal and oils products now."[89]

Interest in biodiesel waned with the development of the ability to derive vast amounts of energy from the much less expensive processes related to fossil fuels. With the refining of crude oil into fractions, based on the oils processing volatility, came a great many energy rich petroleum based products and until just recently rendered biofuels of little interest[90]. Still, some research did occur such as the effort to make thinner plant oil based products that could be used as a fuel in the 1930's and in 1937 G. Chavanne was granted a Belgian patent for an ethyl ester of palm oil, which would now likely be considered the direct ancestor to modern biodiesel.[91]

The only time during the first half of the 20th century wherein any significant demand and/or usage of biodiesel occurred was during the energy crisis that occurred during and immediately after World War II.[92] More recently the rise of environmentalism and the corresponding energy crisis of the 1970's and 80's revived interest in biofuels and renewable energy sources.[93]

"Diesel fuel" to be literal is a fuel that is capable of running in a diesel engine. Therefore, the chemical definitions for diesel fuels have changed over time as both the diesel engine and oil refining techniques have evolved.[94] The significant characteristic of a diesel engine, and its fuel needs, as opposed to those of other internal combustion engines, is that within a diesel engine oxygen is much more highly compressed causing it to heat up and spontaneously react with the injected diesel fuel. As a result of this characteristic, suitable biofuels can be used to replace the normally more volatile fossil fuels as energy sources. Biodiesel itself is a mixture of monoalkyl esters of fatty acids and are generally produced by the transesterfication of triglycerides[95] which themselves come from biological sources such as animal fats and vegetable oils.[96] The oils from these biological sources are extracted or pressed to produce a crude oil that serves as the triglyceride source[97].

2. The Chemistry of Biodiesel and the Transesterfication Reaction

As already noted the production of biodiesel from natural oils is typically accomplished by a transesterfication reaction. Transesterfication is the reaction wherein a triglyceride from fat or oil, aided by a catalyst, reacts with an alcohol to form esters and glycerol[98]. In addition to amyl alcohol the alcohols used can include methanol, ethanol, propanol, and butanol[99].

The general form of the transesterfication reaction, displaying the products and reactants, is shown below (see Figure 17).

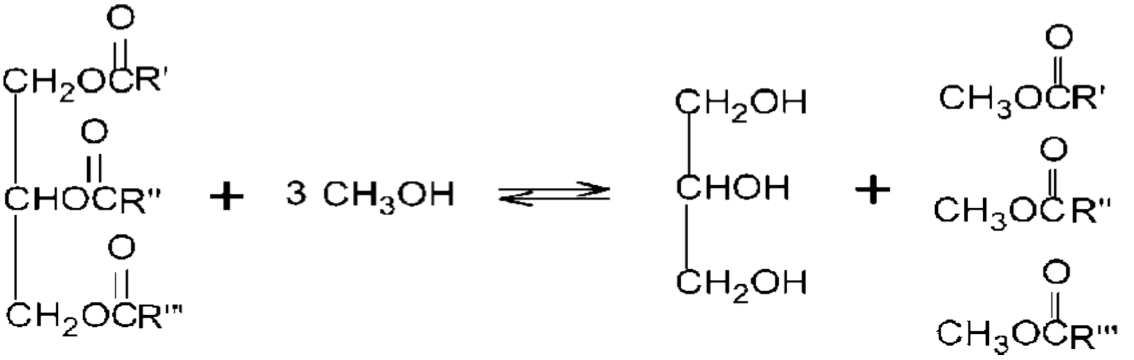


Figure 17. Transesterfication Reaction

In this reaction we can see a triglyceride is reacting with an alcohol, in this case methanol, in a 1:3 ratio to produce glycerol and 3 methyl esters. The methyl esters produced are the biodiesel products that must be separated from the glycerolin biodiesel fuel production.[100] *R groups represent the carbon chains on the triglyceride.*

The different vegetable oils that may be used in biodiesel production can have different chain lengths and saturation states. The boiling and melting points of the resulting fatty acids [methyl esters] increase as the number of carbon atoms contained within the R chains increase, and will decrease with an increasing number of double bonds. Several factors, including the type of catalyst, alcohol to oil ratio, temperature and the purity of the reagents, can also have an influence on the reaction and final products.[101]

3. Catalysts

The commonly used catalysts for transesterfication are either acids or alkalis [bases].[103] Specifically, they are homogenous catalysts that are soluble in the alcohol reactant. [104] The most common alkalis are NaOH and KOH along with their corresponding alkoxides; i.e. sodium ethoxide.[105] There are a number of advantages and disadvantages to either the acid catalyzed or base catalyzed mechanism. While it is possible to do the transesterfication reaction without a catalyst, the reaction must then be performed under critical conditions, i.e. high temperature and/or high pressure, making it much more difficult and/or expensive.

(a) Base Catalysts

To better understand the transesterfication process the base catalyzed mechanism is shown below in Figure 18.

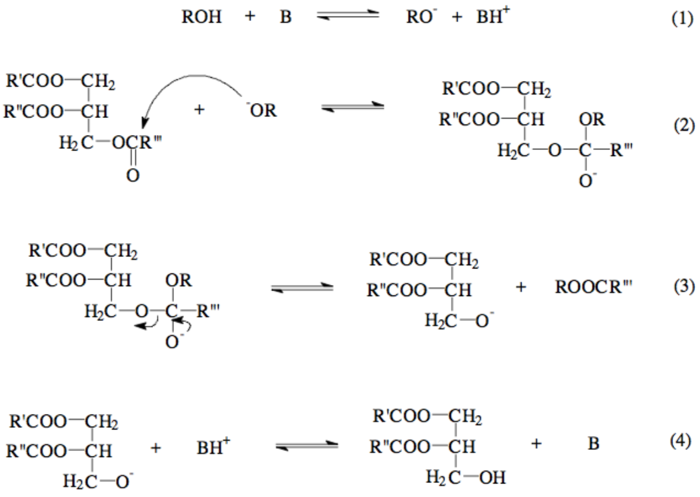


Figure 18. Mechanism of Base Catalyzed Transesterfication[106]

In the first step of this mechanism the base catalyst reacts with the alcohol removing hydrogen from the hydroxyl functional group to form an alkoxide and protonated catalyst [1]. Then the carbonyl group of the triglyceride undergoes a nucliophylic attack by the alkoxide that generates a tetrahedral intermediate [2]. From the tetrahedral intermediate an alkyl ester and corresponding diglyceride anion are formed [3]. The diglyceride anion deprotonates the catalyst, thus forming a neutral diglyceride and allowing the catalyst to react with a second molecule of alcohol, starting another catalytic cycle. The diglycerides and resulting monoglycerides are then converted by the same mechanism to produce a final mixture of alkyl esters, i.e. the biodiesel, and glycerol.[107]

Alkaline Metal Alkoxides [AMAs], the most active of catalysts, have yields as high as 98%, have short reaction times [only 30 minutes in some cases], need only a 0.5% molar concentration to be effective, and are capable of working at low temperatures and low pressures.[108] Alkaline Metal Hydroxides [AMHs], on the other hand, are frequently actually used as catalysts because of their significant lower cost. Although less active then alkoxides, the Hydroxides can give the same conversion rate if a 1-2% molar concentration is used[109]. They have the additional disadvantage, however, of requiring the absence of water.[110] In the presence of water the saponification reaction shown below in Figure 19 will occur:

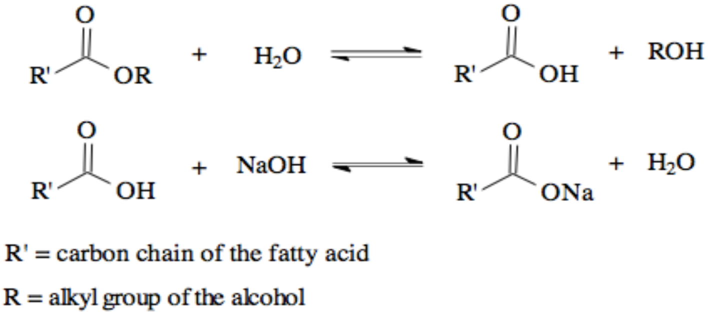


Figure 19. Saponification of Fatty Acid Alkyl Esters

Water hydrolyzes alkyl esters to produce soap.

The presence of water [H2O] allows for the hydrolysis of the alkyl ester, producing soap in a process known as saponification.[111] The production of soap lowers the yield of the esters (i.e. biodiesel) and also makes the separation and recovery of glycerol difficult due to the formation of emulsions.[112] There is often difficulty in recovering the basic catalyst from the initial reaction mixture. Frequently, the most viable way to deal with the presence of a basic catalyst is to neutralize it with an acid following the reactions' completion. Such neutralization can generate a great amount of wastewater.

The fact that the catalyst is not usually recovered from the reaction creates economic and environmental issues. Because many oil extracts are naturally acidic, they can result in more base being required than first expected [first to neutralize the mixtures and then to act as catalysts]. As a byproduct of the neutralization of acid, water is produced in a quantity that depends on the initial acidity of the oil. The water formed can result in increased saponification. Despite the disadvantages stated, the very high activity rate of the base catalyzed reaction, along with the low pressures and temperatures involved in their actions, and the very high yields they generate [possibly greater than 98%], have made this method the most preferred method used for commercially produced biodiesel.

(b) Acid Catalysts

Another method that is sometimes employed in the transesterfication reaction is the acid catalyzed method (see Figure 20).

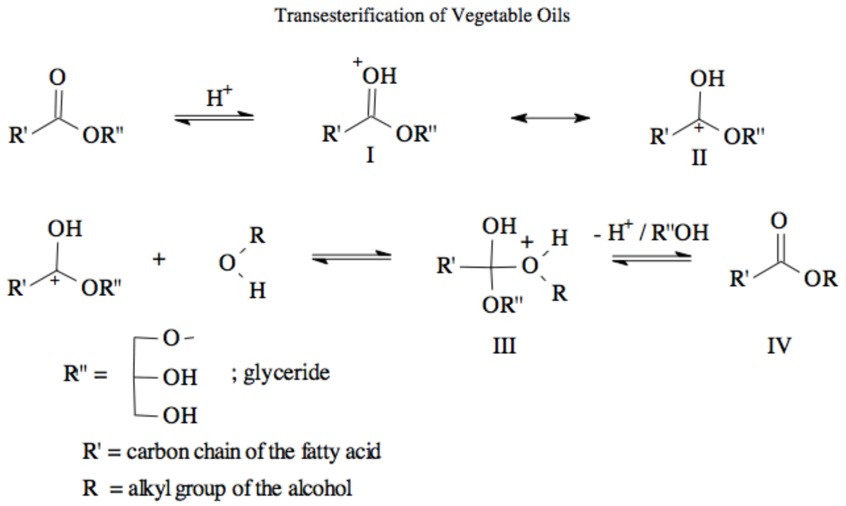


Figure 20. Acid Catalyzed Mechanism of Transesterfication Reaction [113]

This Figure displays the mechanism for an acid catalyzed transesterfication for a mono glyceride, however it can be extended to di and tri glycerides by repeating the same process.

In the acid catalyzed mechanism the carbonyl group of the ester is first protonated from a proton that came from the acid catalyst [I]. This protonation results in a carbocation [II]. This carbocation will then undergo a nucliophylic attack from the electrons on the oxygen of the alcohol to produce a tetrahedral intermediate (III). The tetrahedral intermediate then eliminates glycerol and forms a new ester (IV) that is the biodiesel product, and regenerates the H+ catalyst. [114]

In the acid catalyzed mechanism, sulfonic and sulfuric acids are preferably used.[115] The advantages to the acid catalyzed mechanism include the producing of very high yields [greater then a 99 % conversion being possible]. However, the acid catalyzed method has several significant drawbacks as well; water [H2O] formation is still of concern but to a lesser extent than in base catalyzed reactions. [116] Carboxylic acid may be formed by water reacting with the carbocation suggesting that the presence of water could result in the competitive formation of carboxylic acids. Additionally, the time required for acid catalyzed transesterfication is usually much longer, not unusually requiring more than 3 hours to reach completion [and some reactions may require up to 50 hours for completion] even when higher temperatures and pressures are used. The very high ratio of alcohol to oil also makes this a less efficient technique and the alcohol makes glycerol removal more difficult. On the other hand, as the initial oils extracts are naturally acidic, no additional catalyst to compensate for acidity must be added. The oils' natural acidity may even increase the catalytic ability of the acid catalysts used and, by not having to neutralize these acids, water is not formed as it is in the base catalyzed mechanism.

Regardless of the catalytic method used, a stoichiometric molar ratio of at least 3:1, alcohol to triglyceride is needed. In practice, however, the ratio needs to be higher [more alcohol] to drive the reaction to completion.[117]

(c) Solid State Catalysts

There are currently many problems with the standard process for producing biodiesel fuel. Amongst them are [1] the generation of massive amounts of wastewater needed to remove the usually used basic catalyst and [2] the soap formation that results using the same process.[118] Additionally, the currently preferred method of production, renders the base catalyst required to become more or less unrecoverable. Actually, the current method requires the addition of acid or base to the final product, corresponding to the use of a basic or acidic catalyst respectively,[119] to neutralize the produced biodiesel product. This requirement gives both economic and environmental drawbacks to the commercial production of biofuel. To address some of the above issues chemists have begun research into the possibility of using a heterogeneous solid state transesterfication catalyst to replace the current homogeneous ones. [120]

In recent decades a very wide range of chemicals have been proposed and studied as solid state catalysts. A small sample of these include calcined sodium silicate,[121] Na/NaOH/γ-Al_2O_3,[122] zeolites, metal catalysts, KF/Al2O3, KF/Eu2O3,SO_4^{2-}, vanadyle phosphate, inorganic metal ions, biological enzymes and even calcified egg shells.[123] Although a large number of compounds have been used they can typically be classified as basic, acidic or biological [enzymatic] in nature.[124] Each of these types or classes of catalyst has advantages and disadvantages, and while each class may represent a broad range of compounds, some general conclusions can be drawn about each class.

Solid base compounds, like their homogeneous counterparts, seem to offer advantages over solid acidic compounds, as they have higher catalytic activity and result in a faster reaction rate.[125] They are, however, vulnerable to deactivation by free fatty acids [often present in the vegetable oil used as a substrate], sometimes sensitive to water[126] and requiring of the extreme conditions of both high temperature and high pressures to work effectively.[127]

Solid acid compounds, on the other hand, are insensitive to both free fatty acids and water, but require even higher temperatures for effectiveness and also often the use of more catalyst [loading].[128]

Biological catalysts such as enzymes can be classified as homogeneous, heterogeneous or as a totally separate class of their own. There have been mixed reviews as to the production success rates with their use. High catalytic specificity and an ability to function at near ambient conditions are favorable traits[129] of these catalysts but they are quite expensive[130] and they have a number of other drawbacks traditionally associated with proteins [as they typically are] i.e. pH sensitivity, temperature sensitivity, difficulties isolating them from a biological source and their degradation over time.[131]

(d) Alkaline Earth Metal Oxides and Metal Hydroxides

Two groups of molecules that are now of considerable interest for use as solid state catalysts are metal oxides and metal hydroxides. This includes both alkaline earth metals and transition metals. Alkaline earth metal oxides can act as solid basic metal catalysts.[132] There have been numerous studies devoted to researching the catalytic ability of various alkaline earth metal oxides [133] including MgO, CaO, SrO and BaO.[134] Because these molecules have a significant charge distribution, as well as free electrons to act as a base on the oxygen, it is quite logical that they should be considered when looking for suitable replacement catalysts. It has been found that these compounds can successfully serve as heterogeneous transesterfication catalysts and an over 99% reaction yield has been recorded using them.[135] Additionally, the alkaline earth metal oxides are relatively easy to make and are also quite stable, both qualities making them even more useful as catalysts. While not all metal oxide compounds would traditionally be classified as solid state catalysts due to their solubility in water, it is important to note that it is their solubility in methanol, which is lower, that is of concern for the reactions in question[136]. The currently proposed mechanism for how a transition metal oxide, in this example CaO, catalyzes a reaction is shown in Figure 21.[137]

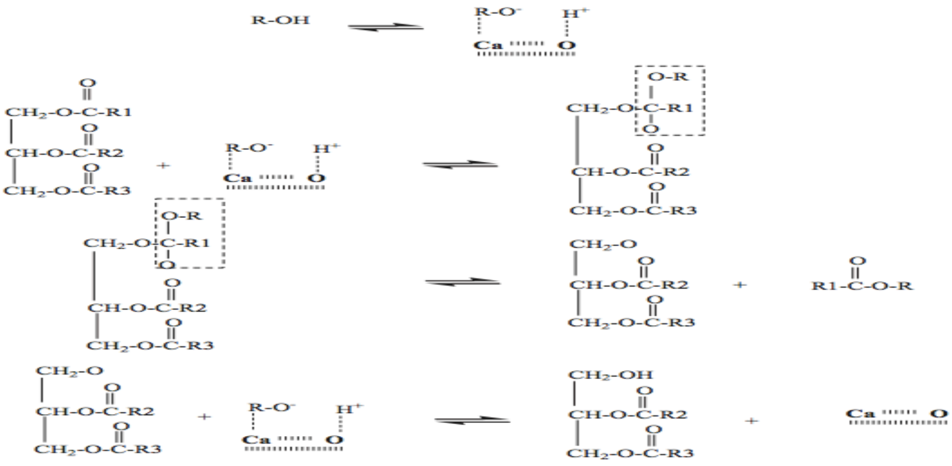


Figure 21. Transition Metal Oxides As Catalysts

In this mechanism it is proposed that the CaO first reacts with the alcohol to produces an alkoxide and protonated catalyst. The carboneale group on the triglyceride then undergoes to a nucliophylic attack from the alkoxide and forms a tetrahedral intermediate. The alkyl ester breaks off to form an anionic diglyceride allowing the diglyceride to deprotonate the catalyst. The catalyst is now free to form a new alkoxide and the process is repeated on the diglyceride and again on the subsequent monoglycerides, eventually removing all of the fatty acids. [138]

The key factor in the catalytic reaction shown above is that the CaO, has a relatively strong base sight, and is therefore able to facilitate separation of the alcohol into RO- and H+.[139]

Using the above mechanism as a basis we can examine why other metal oxides are also able to catalyze the reaction. Many metal oxides such as CuO have active basic sites allowing them to follow this same proposed mechanism. It is also beneficially the case that most transition metal oxides have low solubility and that there are many metallic oxides to choose from. Each of them likely has chemistry, which varies a bit from each other. A significant factor worth noting is that many metal oxides will have both acidic and basic sites on them, while others may act as pure acids. Because of this a different mechanism of catalysis is likely to occur for these two types of metal oxides. As acidic compounds are capable of performing the transesterfication reaction, their potential as solid state catalysts are equally valid. Furthermore the presence of both acidic and basic sites on a single catalyst could even prove advantageous.

Because of this, the number of metal oxides as potential solid state catalysts is not significantly limited. Worth noting is that it is common for metal oxides to be "doped," or used as a mixed metal oxide, to increase their catalytic behavior. [140]

Metal hydroxides are able to act in a manner similar to the basic oxides and can, therefore, also serve as solid state catalysts as well, provided that they are insoluble in the reaction mixture. Evidence of this can be seen in the similar behavior and catalytic activity of Ba (OH)^{2} and Ca (OH)$^{2.}$ [141]

4. Determination of Biodiesel Quality

Once biodiesel has been produced and prior to it being used as a fuel source it must be tested to ensure it meets certain standards of acceptability. A variety of tests can be performed on biodiesel to determine its quality and typically numbers of them are done with gas chromatography [GC]. In an average sample of biodiesel the most important factors determining whether or not it is of commercial grade are it's free and total glycerol content. These two parameters indicate how completely the necessary transesterfication reaction has been and are extremely important to users of the biodiesel; because, high glycerol content can be devastating to any engine within which it is used as a fuel. Glycerol is highly polar, a feature which makes it quite viscous and gel-like. Over time glycerol forms deposits inside engines, gums them up, and ultimately can cause them to break. While gas chromatography is typically used to test for the glycerol content alternate methods have been proposed. The only widely accepted test in the United States for determining the free and total glycerol content of biodiesel is the American Society for Testing and Materials' [ASTM] test D 6584-00 and it does use a GC. Currently, sending a sample of biodiesel to an official facility for a full ASTM testing workup will cost about $2000. Additionally, as several samples of biodiesel are usually required, even from a single batch, for valid testing, the actual expense is typically greater. This expense alone, frequently, makes it cost prohibitive to start even a small scale biodiesel processing plant such as ones that can be beneficial in remote or more rural communities that would like to use their own readily available plant matter for energy. Low quality biodiesel can be quite hazardous to engines and the mere threat of breaking a $200,000 tractor can prevent “home –brewed” biodiesel’s adoption.

A major goal of this research project was to establish an economically feasible facility for biodiesel testing. The costs currently required to test our own James Madison University [JMU] small batch biodiesel products has been almost prohibitive to the expansion of the biodiesel alternative fuel program, my project included. In an attempt to remedy this situation, the ability to test for free and total glycerol, the two most important biodiesel quality tests, at JMU, was made a major part of the research in this project. To understand the testing requirement and the necessary “standard equipment” to replicate or approximate an ASTM biodiesel free and total glycerin test protocol, one must first fully examine and understand exactly how a gas chromatogram [GC] works. The following diagram provides a basic outline of how a typical GC works (see Figure 22).

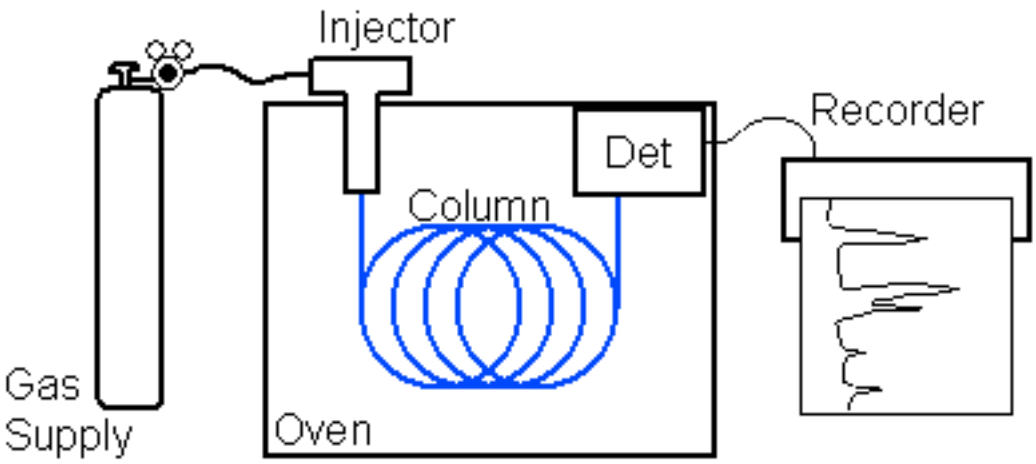


Figure 22: Gas Chromatography Laboratory Setup[142]

GCs are chromatographic devices that are useful for separating and identifying the various components in a mixture. In AGC analytes are moved through a column by a gaseous mobile phase, which is also known as the carrier gas.[143] To work properly it is crucial that the mobile phase gas be chemically inert. Although helium is the most commonly used mobile phase gas, hydrogen is also frequently used. Less frequently, argon or nitrogen is chosen for the carrier work.[144] A sample is first placed into the injector of the column. The injector then helps properly deposit the sample into the column. The column type generally used is a wall coated, open, tubular column. In this type of column there is a thin film that coats the interior wall of the column, making the stationary phase. The column itself is typically only .25 to .53 mm in diameter. The column is housed in a variable temperature oven that helps with the necessary vaporization of the sample. In the column, the sample's components will exist in an equilibrium between the mobile phase and stationary phase with the equilibrium also depending upon the volatility of the analyte. Typically, in this situation, a more volatile sample compound will spend more time in the mobile phase, and a more polar, and therefore less volatile, compound, will be more strongly retained by the column. As the analytes travel through the column they become separated based upon their different equalibria. The column itself is often quite long so as to facilitate adequate separation; sizes typically ranging from 15 to 30 meters. Both shorter, and much longer, columns are available to accommodate the needs of the sample to be measured.

As the analytes elude out of the end of the column they must be detected. A flame ionization detector, or FID, accomplishes this task and is employed to detect and measure the biodiesel. A schematic of a FID is shown below in Figure 23.

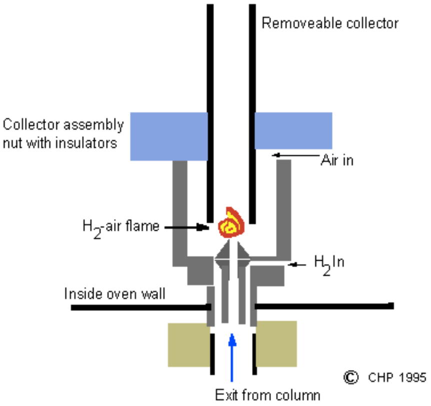


Figure 23. Diagram of a Flame Ionization Detector

The eluent enters from the end of the column into the FID where a hydrogen flame exists. In the hydrogen flame organic compounds will pyrolize and form electrons and ions.[145] These charged particles can then be measured by the current they produce. The current forms because a small voltage of a few hundredths of a volt is applied between the tip of the burner and an electrode above the flame. The breakdown of the original compound makes this a destructive detection technique. The current produced is proportional to the amount of initial carbon in the sample. As a result, the apparatus is categorized as a mass sensing detector rather than a concentration sensing detector.[146]

II. Experimental Method Development

A. Method Progression

The development of the methods and the progression of the project will now be explained. As I was the sole chemist in the ISAT alternative fuel group, deciding on the proper procedures and methodology took the most of my time and energy. The initial step in the project consisted of determining exactly what my project should, or could, include, and precisely how to reasonably manage its scope. By attempting an interdepartmental thesis it meant that I would necessarily need to learn not only the different departmental resources, but also and what would actually, rather than just feasibly, be made available to the project and at my disposal.

It had been decided that I physically be set up in the Alternative Fuel Vehicle Laboratory [AFVL] which, in actuality, is for the most part a mechanic's workshop rather than a chemists' laboratory. So, from the start there was no traditional laboratory or for that matter even a fume hood to work with.

Initially, my professor and mentor, Dr. Bachmann, was most interested in developing a continuous flow processor for biodiesel production and this was very exciting to me as well. Thus, in the first phase of my research experience I had two main focuses; the first was to gain in-depth knowledge of biofuels by extensively reviewing the literature, visiting sites and conducting chemical research and experimentation. I became deeply familiar with the transesterfication reaction and biodiesel production. The second focus was necessarily to become what is called, "Level 3 Certified" in the Mechanics Laboratory[i.e. warehouse] , so that I would be allowed to use and come to better understand the physical considerations that had to be considered in the design of the continuous flow reactor. Level 3 certification is the highest level obtainable, as a student researcher at JMU, and it meant that I had to know how all the small tools worked, how the heavy machinery [such as metal cutting saws] worked, and also how the different cutting torches worked. Additionally, it meant that I had to become proficient with MIG, TIG and acetylene welding torches.

Once certification was successfully accomplished, we attempted experiments with several small batches of substrate to produce biodiesel and to become familiar with the actual reactions involved. We enthusiastically met the numerous challenges of having only a makeshift lab. I learned a great deal about innovation and overcoming frustration. We even had to fit out the exhaust pipes to be used as a fume hood in our best effort to create a safe laboratory setting. I frequently tried to reach into the Chemistry Department for available resources but, at the time, there were actually very few to spare.

It became clear with time that some challenges would be greater than others. A major one was that there were significant steric effects involving the alcohol being used. There were very significant differences observed even between the methanol and the ethanol being used. Additionally, I learned that methanol does not form the same aziotrope with water that ethanol does, and theorized that this was also a key factor causing some difficulties we were encountering as water impurities can cause the saponification reaction described earlier. Familiarization with the reaction led to it becoming clearer to me that the biggest factor inhibiting the production of a continuous flow reactor was the production of glycerol. Glycerol production was commonly and inadequately dealt with by letting it settle out of the biodiesel; that is, by using a simple physical separation [pouring out the glycerol or decanting the biodiesel.] Seeing this issue repeatedly causing problems prompted me to propose that we try to produce a distillation reaction. The higher temperature used in such reactions were heavily favored in the many papers I had reviewed, the reaction rate appeared to be drastically reduced, and I believed the biodiesel could more easily be separated from the glycerol with this technique. Also, if we chose this path the glycerol distillate layer itself could be used to meet some of the energy requirements of the heat source. Some members of the group were against the idea of energy input as it can be considered to be a less environmentally sound and economically friendly method. I attempted to point out that chemically, the reaction probably needed the energy or could at the least use the energy to be pushed to completion and that the likely resulting vastly increased reaction rate would allow for production amounts that would offset energy cost. I reasoned that the technology needed to perform the reaction under these conditions was available and the needed infrastructure already created, so we could also be increasing our potential for success. This debate was a reflection of our different backgrounds and was one of the first attempts we had to “speak each others scientific language.”

It was my belief that the reaction we were attempting could be improved by the means of using a solid state [and therefore recoverable] heterogeneous catalyst as opposed to the unrecoverable homogeneous one that currently dominates production. This option was an area of current research. As the transesterfication reaction is already a two phase reaction, being composed of an oil and an alcohol, adding a heterogeneous catalyst would ordinarily have limited success because it would then make up a third phase, and all three phases would need to be in contact simultaneously for the appropriate reaction to proceed. Recognizing this difficulty, I proposed that we embed a heterogeneous catalyst onto a static mixer so that the three phases would all be brought into contact and therefore effectively solve the issue. I reasoned that this would not only be effective but also could be efficient and used in current small batch systems [such as our own] and/or have the potential to be developed for a continuous flow process. In either case, I felt it would increase the feasibility of biodiesel production, the reaction becomes simpler to perform, and the reaction is both economically and environmentally more friendly than the ones currently being used [and in which the catalyst is not recoverable]. Dr. Bachmann took note and suggested we change the project to focus on the idea.

Extensive research now had to be applied to this new direction. I decided to focus my initial attention to looking for compounds with excess electrons, which could function as bases, while having minimum solubility, and having chemical properties that could also enable them to become embedded onto a surface. I recognized that practically speaking we also would need the compounds chosen for examination to be cost effective and relatively available. The most promising compounds I found were metal oxides and hydroxides. The electron density on the oxygen[s] serve well as Lewis base in many cases and many of these compounds had minimal solubility. Many metal oxides may have acidic sites in addition to their basic sites, or be purely acidic in nature. In any of these scenarios they can potentially perform as transesterfication catalysts. Additionally, some of these compounds were, uncharacteristically, readily available to me, and others such as iron and magnesium oxide could easily be made. As most of these compounds had minimal solubility in water, I inferred that this would also be the case in the less polar methanol, and that this was as easily testable. Also I knew that metal oxides traditionally have quite high melting and vaporization points. I considered this important because many transesterfication reactions are performed under intense heat and I did not want to limit the ability to do so. Additionally, I felt that the high melting points would allow the material to be incorporated into/onto aluminum [or other metal]. Mixing could occur by melting the top layer with a torch and adding it to the molten metal, or by mixing it with clay and firing it in a kiln. With help from the Department of Chemistry appropriate and necessary chemicals for further experiments were obtained. Magnesium was obtained from pure samples of magnesium oxide. It was produced from the metal itself. As the temperature for magnesium ignition is relatively high at 473C, and there was neither a traditional laboratory facility or laboratory high heat generation source available, a creative solution was employed to ignite the magnesium. After a few unsuccessful attempts at ignition, it was found that by placing a small pile of magnesium on a steel table, and then heating the table from below with an acetylene torch, the ignition process could be initiated. The reaction so started actually became hot enough to produce a small secondary thermite reaction wherein the magnesium oxide reacted with small amounts of iron from the welding table to produce iron (III) oxide. I considered this a possibly acceptable impurity as iron oxide was a potential catalyst and there was some literature to support mixing more than one metal to the oxides to boost their catalytic activity.

The next challenge was determining what the appropriate testing conditions should be. I found that most of the literature supported using both high temperature and high pressure conditions. Despite this, the research group decided to test the suggested materials under ambient conditions to reduce energy input. Niobium oxide, cobalt oxide, calcium oxide, copper II oxide, lead dioxide, manganese dioxide, magnesium hydroxide and barium hydroxide were all tested for their catalytic potential. Methanol, vegetable oil and the potential catalysts were mixed together and stirred overnight at room temperature and pressure. It was found that under ambient conditions barium hydroxide successfully catalyzed the transesterfication reaction.

During this period of time it became very apparent that a method for testing the success of the catalysts would definitely be needed. Specifically, we would need to determine the amount of glycerol there was in solution. I examined the issue and suggested the possibility of using a spectroscopic means to measure the concentration of glycerol. The advantages to this method I believed, would include reducing the operating time and having a faster sample measurement time as compared with the more traditional method of using a GC. GC testing however, is currently required by the ASTM and is thus the only way to ensure commercial grade biodiesel. Because of the significance of complying with ASTM protocols and the very high sensitivity and reproducibility of a GC it was easily decided that they were the preferable instrumentation.

I had fully examined the ASTM methods which gave me some initial apprehension about attempting to replicate them on campus. I had run GCs before, but had never attempted to either set one up from scratch or to maintain one. Recognizing that I was the sole chemistry major in our group, and that it was unlikely that Chemistry Department faculty would routinely going to be available, it seemed obvious that this testing would fall to me and that it was going to be a challenge. Furthermore, after examining the ASTM protocols even more closely, I learned that both a derivatization reaction and other unusual conditions might be met and special equipment, such as a high temperature column to run the sample, would be required. I now had to determine what materials would be required to meet actual ASTM standards, including both chemicals, and equipment, what column would be needed, and most importantly what GC availability and ability, did we have and would we need.

The only GC available in ISAT was an SRI 8610. A picture of this instrument is shown below (see Figure 24).

Figure 24. Image of SRI 8610[147]

With the help of SRI technical support, and the identifying features of its knobs, we were able to classify our GC as a 1980s era machine. Specifically, it was an 8610-B. Although quite old by state-of-the-art laboratory standards, some advantages to the machine were discovered when I assessed it. Firstly, it had its own built-in FID, which was very important as an FID was specified as necessary in the ASTM procedure standard. The 8610-B also had its own air compressor which meant (1)that it would require no external air tank for the FID to function, and(2) that the flow rates during experiments could be easily controlled. One less tank of gas to manage was also favorable. Additionally, the GC was also already more or less set up and had its own computer which was running easy to control "peak sample" software. Unfortunately, when tested, the oven within the GC could only reach a maximum temperature of 250 C. As the procedure we were expected to perform required a temperature maximum of 380C, I understood immediately that this could be a significant problem. A low temperature would not only mean that the samples' retention time would increase and its resolution decrease, but also that the heavier molecules in the sample would likely never vaporize, giving it an infinite retention time and could result in clogging the column and damaging it. After some time, and much discussion with both professors and tech support, it was determined that there was no safe way in which we would be able to increase the temperature within the oven and that a new one would therefore need to be found if appropriate experiments were to be completed successfully.

At this point it was necessary to again then turn to the Chemistry Department for some help and support. Dr. Foust graciously agreed to provide the research team with a different GC that he knew of and believed was currently in storage. Once located and examined we found that this GC also had some issues. As time had passed while we attempted to deal with the prior issues described I knew we would need rapid resolution if we were ever to get our experiments completed. An issue immediately noted and of concern was that this GC had most recently been used as a source for parts and would therefore likely need not just careful inspection but also the ability to have any missing parts replaced prior to its use. Thanks to Dr. Ralston, Dr. Downey and the Department of Chemistry we did received the rather intact GC shortly after our meeting with Dr. Faust and we situated it as best possible in the ISAT environmental laboratory. A few major and also many minor hurdles were then overcome as I learned about the significant differences between how an instrument supposedly runs [i.e. the principles that we learn about in class], and the actual intricate details of keeping a well calibrated expensive piece of laboratory equipment up and running. Numerous items needed to be properly and constantly addressed to ensure that the equipment would function well in a critical high temperature experiment.

One of the first issues that needed addressing was that this GC required tanks of the gases hydrogen, helium and oxygen to perform the required ASTM tests. These gases not only needed to be obtained, but also needed to be stored and approved for our use in the ISAT lab where we planned to run our experiments. In short official clearance was needed to be able to set up and use these gases. This was most notably true for the hydrogen. The clearances were obtained.

Next, I discovered that there were some small holes in the GC equipment. Staff advised me that to properly patch and repair the holes I would need to find some high-temperature insulation. I also soon came to learn that the holes seen were vestigial and from prior instrumentation and that there might well be others I had not yet discovered. Fiberglass insulation was ultimately deemed to be sufficient for our patching purposes. The only feasible alternative to fiberglass insulation was hard to locate rock wool.

Perhaps the greatest challenge came next when I needed to enable the donated GC to "speak" to modern computers. This required locating a Data Acquisition Card, a 82341C HP-IB card and a cable capable of first carrying an analogy signal out of the GC and then interfacing it to a modern computer. Software, capable of allowing the computer and the GC to "talk," was obviously also required. Obtaining appropriate software was truly a considerable task as the GC actually had originally used, and was meant to use, software on old floppy discs [the kind that actually were floppy]. The floppy discs were unreadable by any other equipment that we would necessarily be using. Attempts were made to circumvent this issue by using the current peak sample software that was readily available from the SRI Instrumentation. It was not compatible. Because modern programs cost hundreds, if not thousands, of dollars, and no program we knew of was actually guaranteed to work for us, we again were faced with a serious problem that could stop the project in its tracks. It was decided to again examine the old Agelent software to determine if we could somehow manage to enable its' function. With numerous hours of Agelent's technical support, the endless help of ISAT's technical support, and most importantly

Dr. Ralston's great help, the software was coaxed to install and recognize the 5890-B on a modern computer.

Little did I know at this point that my technical support hours had just started to accrue. There was next the repeated need for the required gasses to be properly attached to our apparatus, used, and then detached, over and over again, though out the different stages of the experimental research. This was a repetitive and lengthy process that frequently included the cutting of wires, installing of ferrules, installing and calibrating of pressure gages and performing a variety of leak tests.

Throughout the experimentation, items that had not been considered "necessary" earlier were frequently found to be "required" immediately. This meant that I needed to maintain a constant high level of attention to all the details surrounding the ASTM protocols and our experiments, have a willingness to immediately adapt and be flexible, and simultaneously attempt to ensure the quality of the experimentation. On one occasion, for example, a particularly faulty igniter had to be rapidly removed and replaced. Another example occurred as I had to quickly take the lead on several heat related issues and help manage a research experiment at high temperatures. Some other unique challenges also needed my attention and chemistry background, such as when installing the specific column. It was then discovered that special graphite ferrules were required to make a temperature resistant and airtight seal between the column, the injector, and the detector. Another time, I realized that if when running our experiments at high temperatures, oxygen or moisture managed to get inside the column, it [they] would probably oxidize the stationary phase of the reaction and ultimately ruin the column (this meant rapidly ordering and installing Agelent water and oxygen traps to remedy/prevent this possibility). The installation, however, was no simple matter and required that the helium gas tank be safely disconnected, and then reconnected, before we could proceed (and there is a protocol to be learned for everything).

B. Experimental Technique

At a quite late date those of us involved with the numerous repair jobs learned together that the we in fact had a GC with a split liner and split-splitless injector, rather than a cool on column one, like that which had been specified in the ASTM procedures. A cool on column injector is a very different but straightforward device. This device is shown in Figure 25.

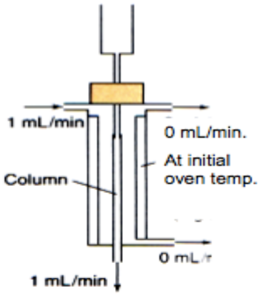


Figure 25. Diagram of a Cool On Column Injector

With an on column injector, the inlet guides the injection needle so that it deposits a sample directly into the column itself. This is useful for our specific experiments that involved the very high boiling temperatures of glycerol in biodiesel. These temperatures can in fact be so high that derivatization is required prior to injection. A diagram of the injection technique is shown below in Figure 26.

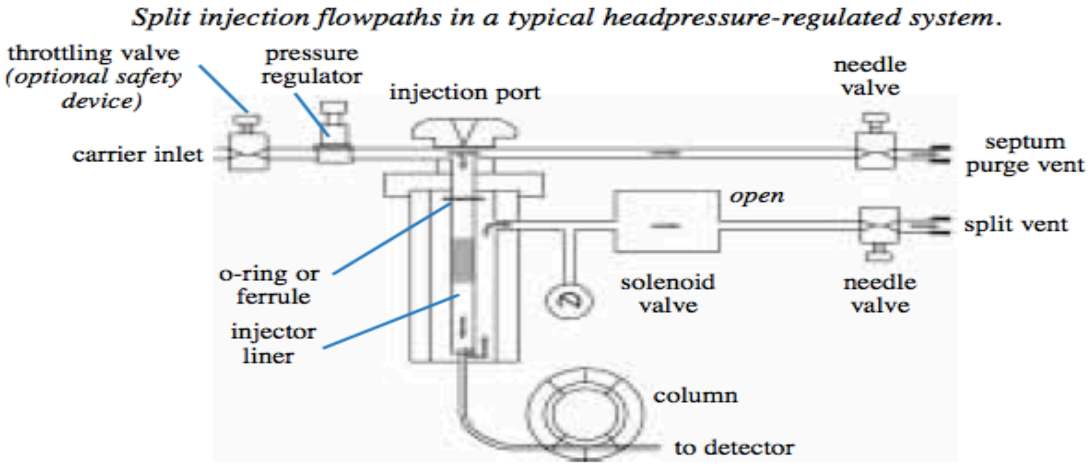


Figure 26. Diagram of split injector when injection is being performed

In a split-splitless injector the liner used determines if the injector operates in split or splitless mode. The liner that we had installed was split. In a split injection the sample is heated at the inlet. Gas flows through the liner chamber and removes about 98% of the sample.[148] Our split liner itself contained a small amount of glass wool upon which compounds with high boiling points were theoretically supposed to condense so that they would not clog the column during an experimental run. Unfortunately, this also this meant that accurate measurements of the glycerol content could not be made as much of it would either condense on to the glass wool or be removed through the split vent. Generally speaking, this also meant that the more volatile compounds would enter the column in disproportionately greater amounts than planned. I initially attempted to remedy this deficiency by finding a replacement direct on column.   This did not result in success, but after considerable research into the matter, I proposed a new method that I believed would allow us to continue making some forward progress with our research experimentation: a linear detection response seemed possible to obtain by using a splitless injection as shown in Figure 27.

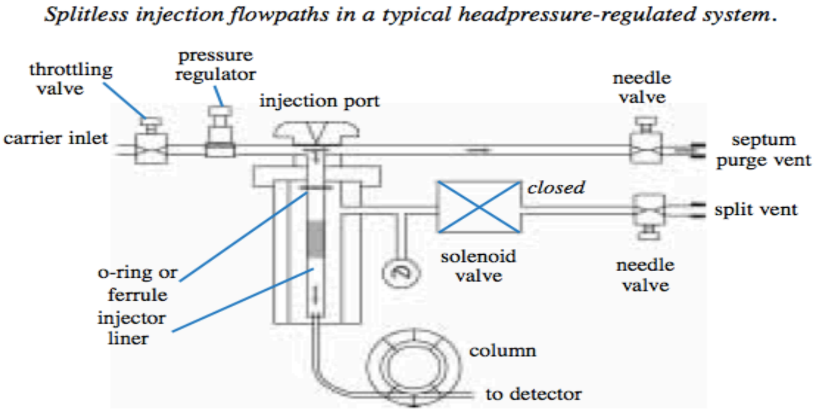


Figure 27. Diagram of Splitless Injection Technique

Splitless injection is similar to split injection, the difference being that there is no gas carrying off the majority of the sample that has been injected in the liner. The liner that I ultimately decided to use was a deactivated glass liner with a chamber having sufficient volume to support the expansion of the biodiesel as a gas, and that was tapered at its distal end so that none (or at the worst an insignificant amount) of any sample with high boiling points would get trapped (at the small area where the column is fed up into the liner). The liner I selected also specifically lacked any sort of glass filter upon which the sample could condense and cause measurement error. The inlet itself was to be set at 390 C, chosen as 390 degrees should be at least 10 degrees higher than the highest potential boiling point of compounds in the biodiesel. During the injection, the column itself was to be at 50 C, and therefore in accordance with ASTM methodology. It was hoped that the biodiesel sample would first vaporize and then condense onto the column head. High temperature septa were also required so as to reduce septa-bleed during the procedure that could in turn cause erroneous peaks and clog the column. Once the installation of the liner was complete, the column was reattached and leak tests were performed.

Next, flow rates were established and, as the machine operated under constant pressure rather than constant flow, flow tests were required for the carrier gas, the auxiliary gas, the hydrogen, the compressed oxygen and the split and the purge vents. The late discovery of a leak in the purge vent further complicated the process but is being managed.

Flow rates were next established at 50C in accordance with the ASTM protocol. However, in a constant flow device, the flow rate decreases substantially as temperatures increase, so the flows were at times difficult to maintain. At the maximum operating temperature used the flow rate is only a fraction of the original 3 mL per minute.

III. Results

The following potential metal oxide and metal hydroxide catalysts were tested for their ambient catalytic activity: magnesium hydroxide, manganese dioxide, lead dioxide, copper (II) oxide, calcium hydroxide, cobalt oxide, niobium oxide, and barium hydroxide. A photograph of these reaction mixtures is displayed in Figure 28.

Figure 28. Image of Reaction Mixtures

The reaction mixtures were prepared the previous night. Solutions labeled from left to right are niobium oxide, cobalt oxide, calcium oxide, copper II oxide, lead dioxide, manganese dioxide, magnesium hydroxide and barium hydroxide. On the far right are the two control KOH catalyzed reactions.

Of the potential catalysts tested only barium hydroxide was observed successfully completing the transesterfication reaction. The barium, glycerol and biodiesel produced in this transesterfication reaction were successfully separated by centrifuging the product mixture. An image of the successfully completed reaction components is shown below (see Figure 29).

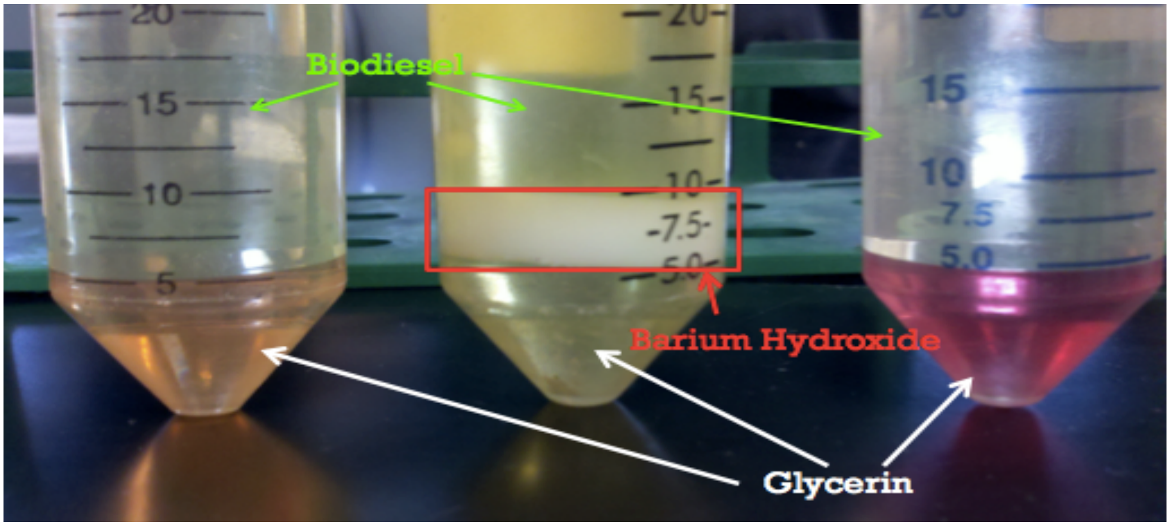


Figure 29. Image of Completed Reaction Components

In this picture the successful production of biodiesel can be seen. The tubes on either side were control reactions in which the biodiesel was produced using traditional KOH dissolved in methanol as the catalyst: biodiesel can be seen on the top of each tube with the denser glycerol layer underneath. The glycerol is lightly dyed. The products of the barium hydroxide catalyzed method can be seen in the center tube: a layer of biodiesel is on top, followed by a layer of barium hydroxide and then glycerin. Product mixtures were centrifuged following their reactions. Centrifuging resulted in the clean separation of products observed.

IV. Discussion

Future work should be performed to determine if there was even minimal solubility of the barium hydroxide within the reaction mixture. If this did occur it might well be inconsequential and an extremely small result of the surface binding method. Currently research is being performed attempting to coat various substances with barium hydroxide for subsequent use as a solid-state catalyst. In the current method the barium hydroxide is dissolved into water, in which it is sparingly soluble, and then precipitated onto the surface of a material. Although coating attempts have occurred using a variety of materials, including plastics, wood and glass, there have been no positive results in which the barium hydroxide has remained firmly attached to the template.

As of the writing of this thesis, the state of testing samples and experimentation by GC is as follows: The GC currently communicates with and can be controlled by the computer program. The column is installed and has been conditioned for running at high temperatures. Hydrogen, helium and oxygen tanks have been attached to the column and all of their connections are currently sealed and leak-free. Helium is being used as both the carrier gas and the auxiliary gas in both the GC and the FID because with potential leaking being an ongoing risk a Helium system was considered a safer set up than a hydrogen one. The column has a high temperature septa installed and there is a functional splitless deactivated glass liner with no glass wool or similar filter installed. Flow tests have been performed on all gasses, at the FID outlet, the split and the purge vents. The purge vent currently is believed to have a small leak and requires replacement. Once this leak is eliminated reproducible samples should be achievable. All the required chemicals and reactants needed to test biodiesel in accordance with ASTM protocols, including the MSTFA derivatization silylating reagent, have been obtained.

V. Conclusion

An interdisciplinary research project brings unique challenges of personnel, equipment, and philosophy that must be successfully navigated for forward progress is to be made. Although the challenges in this project were largely met, they were greatly under estimated at the projects onset and have repeatedly caused delay and reassessment . They have also brought creative thought, the deep learning of the benefits of perseverance, and as strong measure of humility.

New procedures and an invention have been proposed that could improve the biodiesel production and testing regiment.

Endnotes

---

[1] History of Energy | The Franklin Institute, April 25, 2006.

www.fi.edu/learn/case-files/energy.htmT

[2] Biomass Energy Data Book, U.S. Department of Energy

Biomass Energy Data Book

cta.ornl.gov/bedb/index.shtml

Sep 30, 2011 – *Biomass Energy Data Book*: Edition 4

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

Central Intelligence Agency- CIA - The *World Factbook*

https://www.cia.gov/library/publications/the-world-factbook/.../xx.ht.

[3] Statistical Review of World Energy 2011 | BP

www.bp.com/sectionbodycopy.do?categoryId=7500&contentId=

[4] Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

Vaclav Smil, *Energy in World History* (Boulder, CO: Westview Press, 1994),

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

Global Energy Systems Transition, (% of market)

people.hofstra.edu/geotrans/eng/ch8en/.../energytransition.html

[5] The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

Louis C. Hunter and Lynwood Bryant, *A History of Industrial Power in the United States, 1780-1930*, vol. 3, *The Transmission of Power* (Cambridge, MA: The MIT Press, 1991)

[6] Vaclav Smil, *Energy in World History* (Boulder, CO: Westview Press, 1994),

Lewis C. Hunter, *A History of Industrial Power in the United States, 1780-1930*, vol. 1, *Waterpower in the Century of the Steam Engine* (Charlottesville: University of Virginia Press, 1979)

[7] Brooke Hindle and Steven Lubar, *Engine's of Change: The American Industrial Revolution, 1790-1860* (Washington, D.C.: Smithsonian Institution Press, 1986

[8] History of Energy | The Franklin Institute .April 25, 2006..

www.fi.edu/learn/case-files/energy.htmT

Statistical Review of World Energy 2011 | BP

www.bp.com/sectionbodycopy.do?categoryId=7500&contentId=

Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

[9] Carnegie Institution of Washington

---

http://carnegiescience.edu/

*carnegiescience.edu/.../fossil_fuels_earth_*

[10] *Institute for Energy Research*

www.instituteforenergyresearch.org/

US EIA/ http://www.instituteforenergyresearch.org/wp-content/uploads/2008/05/fossil-energy-consumption

[11] *Institute for Energy Research* [Program on Energy and Sustainable Development Working Paper #9, November 2002]

[12] Statistical Review of World Energy 2011 | BP

www.bp.com/sectionbodycopy.do?categoryId=7500&contentId=

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[13] Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

---

[14] 2009 Snapshot of U.S. Energy Use by Lawrence Livermore National Laboratory

Michael Graham Richard

Energy / Renewable Energy

August 24, 2010

Image: Lawrence Livermore National Laboratory

[15] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

[16] The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[17] Institute for Energy Research | 2010 *Annual Energy Review*

www.instituteforenergyresearch.org/.../2010-annual-energy-review/

[18] History of the Oil Industry

www.sjvgeology.org/history/index.html

The Early Days of the History of the Oil Industry - by Samuel T. Pees] 6/2/2004

[19] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

[20] Peak *Oil*: The *End* of the *Oil* Age *www.oildecline.com/*

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[21] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

Peak *Oil*: The *End* of the *Oil* Age *www.oildecline.com/*

[22] *Statistical Review* of World Energy 2011 | *BP*

www.bp.com/statisticalreview

[23] Published May 20 2007 by Energy Bulletin,] .

[24] Total *Energy* - Data - U.S. *Energy Information Administration* (*EIA*)

205.254.135.24/totalenergy/data/annual/

http://www.eia.gov/petroleum/gasdiesel/

[25] Total *Energy* - Data - U.S. *Energy Information Administration* (*EIA*)

205.254.135.24/totalenergy/data/annual/

[26] *Statistical Review* of World Energy 2011 | *BP*

www.bp.com/statisticalreview

Total *Energy* - Data - U.S. *Energy Information Administration* (*EIA*)

---

[27] The Early Days of the History of the Oil Industry - by Samuel T. Pees] 6/2/2004

Transportation Energy Data Book

*cta.ornl.gov/data/*Cached - Similar

Jul 25, 2011 – *Transportation Energy Data Book*: Edition 30. Edition 30 Released June 25, 2011.

[28] [Peak *Oil*: The *End* of the *Oil* Age*www.oildecline.com/*

[29] *Transportation Energy Data Book*

*cta.ornl.gov/data/*Cached - Similar

Jul 25, 2011 – *Transportation Energy Data Book*: Edition 30. Edition 30 Released June 25, 2011.

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[30] Department of Energy data book

[31] Department of Energy *Transportation Energy Data Book*

*cta.ornl.gov/data/*Cached - Similar

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[32] GDP & Oil Prices | Matthew Millar | FINANCIAL SENSE

www.financialsense.com/.../matthew-millar/gdp-and-oil-prices -

What Is GDP?

By Kimberly Amadeo,

[33] Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[34] Total *Energy* - Data - U.S. *Energy Information Administration* (*EIA*)

205.254.135.24/totalenergy/data/annual/

Transportation Energy Data Book

*cta.ornl.gov/data/*Cached - Similar

Jul 25, 2011 – *Transportation Energy Data Book*: Edition 30. Edition 30 Released June 25, 2011

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[35] Carnegie Institution of Washington

http://carnegiescience.edu/

Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

[36] The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

Statistical Review of World Energy 2011 | *BP*

---

www.bp.com/statisticalreview

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[37] The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[38] Energy Transitions - Publisher: Praeger (2010-05-26)

[39] *Statistical Review* of World Energy 2011 | *BP*

www.bp.com/statisticalreview

International Association for Energy Economics, June 23, 2010

www.iaee.org/en/index.aspx

[40] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

Statistical Review of World Energy 2011 | *BP*

www.bp.com/statisticalreview

History of the Oil Industry

www.sjvgeology.org/history/index.html

[41] *BP Statistical Review of World Energy 2010*

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

[42] Transportation Energy Data Book

US Department of Energy

Jul 25, 2011 – *Transportation Energy* Data Book: Edition 30. Edition 30 Released June 25, 2011.

http://cta.ornl.gov/data/download30.shtml

[43] Global Energy Consumption- data source- *BP Statistical Review of World Energy 2010*

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

[44] U.S. Energy Information Administration *Short-Term Energy Outlook*

205.254.135.7/forecasts/steo/pdf/steo_full.pdf

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

[45] *BP Statistical Review of World Energy 2010*

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

[46] U.S. Energy Information Administration *Short-Term Energy Outlook*

205.254.135.7/forecasts/steo/pdf/steo_full.pdf

Total *Energy* - Data - U.S. *Energy Information Administration* (*EIA*)

205.254.135.24/totalenergy/data/annual/

[47] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

BP Statistical Review of World Energy 2010

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

Energy Transitions – History, Requirements and Prospects (publisher: preager, 2010-05-26)

[49] *Energy Transitions – History, Requirements and Prospects (publisher: preager, 2010-05-26)*

CIA - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

---

[51] Barbour, et al., *Energy and American Values*, p. 3.

Energy and American values

Ian G. Barbour, National Humanities Center (U.S.)

0 Reviews

Praeger, 1982 –

Sustainable Energy – without the hot air

David J.C. MacKay 2010

[52] *BP Statistical Review of World Energy 2010*

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

[53] *BP Statistical Review of World Energy 2010*

www.bp.com/.../bp.../statistical_energy_review.../2010.../statistical_re.

[54] The US military oil consumption

by Sohbet Karbuz

www.energybulletin.net/node/13199

International Association for Energy Economics

[55] IAE

[56] The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[International Association for Energy Economics] We Can Live With a Fossil Fuel Future: Oil, Gas, Coal & Shale Oil By Gerald T. Westbrook

International Association for Energy Economics Spring Quarter 2009 p15= p39

We Can Live With a Fossil Fuel Future: Oil, Gas, Coal & Shale Oil

---

By Gerald T. Westbrook*

[57] H2g2 Edited Energy Guide 2006

Atmospheric Pollution from the Internal Combustion Engine in the Urban Environment

http://h2g2.com/dna/h2g2/A16407173

Dec 4, 2006

[58] Summary of Energy Policy Act | Laws and Regulations | US EPA

www1.eere.energy.gov/femp/regulations/epact2005.html

[59] [PDF] ENERGY POLICY ACT OF 2005

[60] Biofuels, Biodiesel and Ethanol - The New York Times

topics.nytimes.com/.../biofuels/index.html

[61] Vaclav Smil, *Energy in World History* (Boulder, CO: Westview Press, 1994), Energy Transitions V. Smil,Publisher: Praeger (2010-05-26)

Energy Transitions

Biodiesel and Ethanol

topics.nytimes.com/.../biofuels/index.html

[62] *CIA* - The World *Factbook*

https://www.cia.gov/library/publications/the-world-factbook

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[63] Department of Energy

Alternative Fuels and Advanced Vehicles Data Center

http://www.afdc.energy.gov/afdc/about.html

---

[64] US Department of Energy: Energy Efficiency & Renewable Energy

http://www.eere.energy.gov/

http://www.afdc.energy.gov/afdc/about.html

[65] Showroom of Automotive History: The Model T

[66] From the Fryer to the Fuel Tank: The Complete Guide to Using ... - Page 23

By Joshua Tickell, Kia Tickell - 2003

[67] The Little Green *Data Book* 2010: Book 2010 - Page 231

world bank, world bank group – 2010

[68] The Energy Story - Chapter 8: *Fossil Fuels* - Coal, Oil and Natural Gas

www.energyquest.ca.gov/story/chapter08.htm

[69] Fuels and Engines:

Technology, Energy, Environment, Volume 2

Jean-Claude Guibet, Emmanuelle Faure-Birchem

Editions OPHRYS, 1999

[70] What is the difference between *diesel fuel* and regular *gasoline* ...

*ask.cars.com/2008/04/diesel-and-gaso.html*Cached - Similar

Apr 23, 2008

[71] *Why Use* Diesel? Advantages and Benefits - How *Diesel Engines* ...

www.dieselserviceandsupply.com/why_use_diesel

[72] Biomass Program: Biomass 2011: Replace the Whole Barrel ...

... areas, such as feedstock supply, conversion pathways, algal biofuels ... It is the policy of the Department of Energy to provide full access to all content from its ...

www1.eere.energy.gov/biomass/biomass_2011.html

---

[73] Energy Independence and Security Act of 2007

Energy Independence and Security Act of 2007. Enacted December 19, 2007 The Energy Independence and Security Act (EISA) of 2007 (Public Law 110-140) aims to improve ...

www.afdc.energy.gov/afdc/laws/eisa

The Geography of Transport Systems

By Jean-Paul Rodrigue, Claude Comtois, Brian Slack

Published May 18th 2009 by Routledge

[74] Next generation biofuels feedstocks USA

Identifying the feedstocks with most potential

San Francisco, USA: 16—17, November 2009

[75] James Madison University Alternative Fuel Vehicle Laboratory and 25X25 Grant

[76] ASTM D6751 - 11b Standard Specification for Biodiesel Fuel

www.astm.org/Standards/D6751.htm

[77] Internal Combustion Engines for Cars

www.articlesbase.com/cars-articles/internal-combustion

[78] How Do Diesel Engines Work?

By Deanna Sclar

content/how-do-diesel-engines-work.html

[79] Biodiesel Fact Sheets - National Biodiesel Board

www.biodiesel.org/resources/fuelfactsheets/default.shtm

Diesel Fuel Quality Is A Question Not A Guarantee

By: John T. Nightingale

http://www.talewins.com/travelwrite/dieselfuel.htm

---

[80] Diesel Fuel Characteristics and use

dodgeram.org/tech/dsl/FAQ/diesel_fuel.htm

[81] Biodiesel as a Lubricant

www.easterngreenway.ca/factsheets/8.html

[82] Biodiesel Fact Sheets - National Biodiesel Board

www.biodiesel.org/resources/fuelfactsheets/default.shtm

[83] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15. (marine biodiesel)

[84] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.(marine biodiesel)

[85] (heterogeneous catalyst system- kwan-young Lee)Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15..

[86] Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378

[87] Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378

[88] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[89] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210. .

[90] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15. Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

---

[91] (History of biodiesel).

[92] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[93] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210. (History of Biodiesel).

[94] Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378

[95] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210. (Heterogeneous catalyst system- Kwan-Young Lee)

[96] Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378

Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[97] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[98] Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378

Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[99] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[100] Santacesaria,E.; Pengmei, L.; Tesser, R.; Serio, M. Heterogeneous catalysts for biodiesel production. Energy and Fuels 2008, 22, 207-217.

---

[101] (Transesterfication of Vegetable Oils Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[103] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210. Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011..

[104] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011..

[105] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15. Fang,Z.; Guo,F. Wei, N.; Xiu,Z. Transesterfication mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Elsevier Journal* 2011, 08.064. (Inorganic Heterogeneous Catalysts Zanzi)

[106] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[107] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[108] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011. Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[109] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

---

[110] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[111] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[112] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011. Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[113] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[114] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[115] Vargas, B.; et al. Transesterification of Vegetable Oils: a Review. J. Braz. Chem. Soc. 1998, 9, 199-210.

[116] Hanna,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[117] Hannab,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

[118] (Hidaka)Korstad, J.: Sharma,Y.C.; Singh,B. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from Pongamia piñata oil. Energy Fuels 2010, 24, 3223-3231.

[119] Hanna,M.; Fangrui, M. Biodiesel production: a review 1. Bioresource Technology 1999, 70, 1-15.

---

[120] Fang,Z.; Guo,F. Wei, N.; Xiu,Z. Transesterfication mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. Elsevier Journal 2011, 08.064.

[121] Fang,Z.; Guo,F. Wei, N.; Xiu,Z. Transesterfication mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. Elsevier Journal 2011, 08.064.

[122] Deong, K.; Lee, J.; Lee, K.; Park, Y.; Kim, M.; Kang, B.; Kim, H.; Transesterfication of vegetable oil to biodiesel using heterogeneous base catalyst. Elsevier Journal 2004, 06.007.

[123] (Santacesarina)(Shaema et al)Deong, K.; Lee, J.; Lee, K.; Park, Y.; Kim, M.; Kang, B.; Kim, H.; Transesterfication of vegetable oil to biodiesel using heterogeneous base catalyst. Elsevier Journal 2004, 06.007..

[124] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[125] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[126] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[127] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[128] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[129] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[130] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

---

[131] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[132] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[133] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[134] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[135] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[136] (Bunyakiat)

[137] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. *Elsevier Journal*

[138] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[139] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[140] Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Elsevier Journal 2011, 6.011.

[141] Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. Elsevier Journal

[142] http://www.kutztown.edu/acad/chem/instruments_html/gc.htm

---

[143] Skoog, D; Holler, J; Crouch, S. Principles of instrumental analysis 6th edition. Thomson Brooks/Cole, 2007

[144] Skoog, D; Holler, J; Crouch, S. Principles of instrumental analysis 6th edition. Thomson Brooks/Cole, 2007

[145] Skoog, D; Holler, J; Crouch, S. Principles of instrumental analysis 6th edition. Thomson Brooks/Cole, 2007

[146] (lecture, notes)

[147] http://www.srigc.com/company.htm

[148] Skoog, D; Holler, J; Crouch, S. Principles of instrumental analysis 6th edition. Thomson Brooks/Cole, 2007

Bibliography

1. The Franklin Institute. *History of Energy*. [Online] April 25, 2006. www.fiedu/learn/case-files/energy.htmT (accessed March 1, 2012).
2. United States Department of Energy. *Biomass Energy Data Book*. [Online] September 30, 2011. 4th ed. www.cta.ornl.gov/bedb/index.shtml (accessed March1, 2012).
3. Rodrigue, J.P., Comptois, C., Slack, B. The Geography of Transport Systems, 2nd ed.; Routledge: New York, 2009.
4. Central Intelligence Agency. *The World Factbook*. www.cia.gov/library/publications/theworldfactbook/.../xx.ht (accessed February 27, 2012).
5. British Petroleum Company. *Statistical Review of World Energy 2011 /BP*. www.bp.com/sectionbodycopy.do?categoryld=7500&contentld= (accessed February 27, 2012).
6. United Stated Department of Energy. *Transportation Energy Data Book*. [Online] July 25, 2011. 30th ed. www.cta.ornl.gov/data/download30.shtml (accessed March 1, 2012).
7. Smil, V. *Energy in World History*; Westview: Boulder, 1994.
8. Rodrigue, J. Global Energy Systems Transition, (%of market). www.peoplehofstra.edu/geotrans/engch8en/.../energytransition.html
9. Hunter, L.C.; Bryant, L. *A History of Industrial Power in the United States, 1780-1930, vol. 3, The Transmission of Power*; MIT: Cambridge, 1991.
10. Hunter, L.C. *A History of Industrial Power in the United States 1780-1930, vol.1, Waterpower in the Century of the Steam Engine*; University of Virginia: Charlottesville, 1979.

---

11. Hindle, B.; Lubar, S. *Engines of Change: The American Industrial Revolution, 1790-1860*; Smithsonian Institution: Washington, D.C., 1986.
12. Institute for Energy Research. 2010 Annual Energy Review. www.instituteforenergyresearch.org/.../2010-annual-energy-review/ (accessed February 24, 2012).
13. Pees, S. *History of the oil Industry*. San Joaquin Valley Geology. www.sjvgeology.org/history/index.html (accessed March 3, 2012).
14. Peak Oil Info and Strategies: *The End of the Oil Age*. www.oildecline.com/
15. Energy Information Administration. Total Energy: Data. http://www.eie.gov/petroleum/gasdiesel/ (accessed February 24, 2012).
16. Pees, S. *The Early Days of the History of the Oil Industry*. San Joaquin Valley Geology. www.sjvgeology.org/ (accessed March3, 2012).
17. Millar, M. GDP & Oil Prices. *Financial Sense*. [Online] March 1, 2011. www.financialsense.com.../matthewmillar/gdp-and-oil-prices- (accessed February 4, 2012).
18. Carnegie Institution of Washington. http://carnegiescience.edu (accessed February 4, 2012).
19. Smil, V.; *Energy Transitions History, Requirements, Prospects*; Praeger: Westport, 2010.
20. International Association for Energy Economics. [Online] June 23, 2010. www.iaee.org/en/index.aspx (accessed February 4, 2012).
21. U.S. Energy Information Administration. *Short-Term Energy Outlook*. http://205.254.135.7/forecast/steo_full.pdf (accessed February 5, 2012).
22. Barbour, I., Brooks, H., Lakoff, S., Opie, J.; Energy and American Values; Praeger, Westport, 1982.

---

23. MacKay, D.; *Sustainable Energy-without the hot air*; UIT Cambridge Ltd.: Cambridge, England, 2009.
24. Karbuz, S.; The US Military Oil Consumption. *Energy Bulletin* [Online] 2006, www.energybulletin.net/node/13199 (accessed February 4, 2012).
25. Westbrook, G.; We Can Live With a Fossil Fuel Future: Oil, Gas. Coal & Shale Oil; International Association for Energy Economics [Online] Spring 2009. www.iaee.org/en/publications/newsletterdl.aspx?id=85 (accessed February 4, 2012).
26. H2g2 Edited Energy Guide. Atmospheric Pollution from the Internal Combustion Engine in the Environment. [Online] 2006. http://h2g2.com/dna/h2g2/A16407173 (accessed February 11, 2012).
27. United States Department of Energy. Energy Efficiency and Renewable Energy: Energy Policy Act. www.eere.energy.gov/femp/regulations/epact2005.html (accessed February 11, 2012).
28. Biofuels, Biodiesel and Ethanol. *The New York Times*, [Online] June 2011. http://topics.nytimes.com/top/news/business/energy-environment/biofuels/index.html (accessed February 11, 2012).
29. United States Department of Energy. Energy Efficiency and Renewable Energy: Alternative Fuels and Advanced Vehicles Data Center. www.afdc.energy.gov/afdc/about.html (accessed February 11, 2012).
30. The Henry Ford. Showroom of Automotive History: The Model T. www.hfmgv.org/exhibits/showroom/1908/model.t.html (accessed January 29, 2012).
31. Tickell, J. *From the Fryer to the Fuel Tank: The Complete Guide to Using Vegetable Oil as an Alternative Fuel*. Tickell Energy Consulting: Tallahassee, 2000.

32. World Bank. *The Little Green Data Book 2010 (World Development Indicators)* World Bank Group: Washington, D.C., 2010.
33. California Energy Commission. The Energy Story: Fossil Fuels - Coal, Oil and Natural Gas. [Online] www.energyquest.ca.gov/story/chapter08.htm (accessed February 4, 2012)
34. Guibert, J. *Fuels and Engines: Technology Energy Environment volume 2,* Eng. Trans.; *Institute français du petrole* publications: Paris, 1999.
35. Ask Cars. What is the difference between diesel fuel and regular gasoline?. [Online] 2008. www.askcars.com/2008/04/diesel-and-gaso.html (accessed January 29, 2012).
36. Diesel Service and Supply. Why Use Diesel? Advantages and Benefits. [Online] 1999. www.dieselserviceandsupply.com/why_use_diesel (accessed January 29, 2011)
37. United States Department of Energy. Energy Efficiency and Renewable Energy: Biomass Program 2011. www.eere.energy.gov/biomass/biomass_2011.html (accessed February 11, 2012).
38. United States Department of Energy. Energy Efficiency and Renewable Energy: Energy Independence and Security Act of 2007. www.afdc.energy.gov/afdc/laws/eisa (accessed February 11, 2012).
39. Bryant, C.; Oh, D.; *et al. Next Generation Biofuels Feedstocks USA,* Greenpower Conferences, San Francisco, CA, November 16-17, 2009.
40. James Madison University. Alternative Fuel Vehicle Laboratory. www.cisat.jmu/biodiesel/index/html
41. ASTM International. Standard Specification for Biodiesel Fuel. www.astm.org/Standards/D6751.htm (accessed February 3, 2012).

---

42. P. Geist. Internal Combustion Engines for Cars. *Articlesbase* [Online] January 2011.
43. (accessed January 29, 2012).
44. Sclar, D. *Auto Repair for Dummies;* 2nd ed.; Wiley: Hoboken2009.
45. Dodge Ram. Diesel Fuel: Characteristics and use. www.dodgeram.org/tech/dsl/FAQ/diesel_fuel.htm (accessed February 5, 2012).
46. Eastern Greenway Oil. Biodiesel as a Lubricant. www.easterngreenway.ca/factsheets/8.html (accessed February 5, 2012).
47. National Diesel Board. Biodiesel Fact Sheets. www.biodiesel.org/resources/fuelfactsheets/default.shtm (accessed February 5, 2012).
48. Korstad, J.: Sharma,Y.C.; Singh,B. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from *Pongamia piñata* oil. *Energy Fuels* 2010, 24, 3223-3231.
49. Hanna,M.; Fangrui, M. Biodiesel production: a review 1. *Bioresource Technology* **1999**, 70, 1-15.
50. Fang,Z.; Guo,F. Wei, N.; Xiu,Z. Transesterfication mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Elsevier Journal* 2011, 08.064.
51. Deong, K.; Lee, J.; Lee, K.; Park, Y.; Kim, M.; Kang, B.; Kim, H.; Transesterfication of vegetable oil to biodiesel using heterogeneous base catalyst. *Elsevier Journal* 2004, 06.007.
52. Santacesaria,E.; Pengmei, L.; Tesser, R.; Serio, M. Heterogeneous catalysts for biodiesel production. *Energy and Fuels* 2008, 22, 207-217.
53. Zanzi, R.; Kiros, Y.; Endalew, A. Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. *Elsevier Journal* 2011, 6.011.

54. Ravindra, P.; Chan, C. Studies on design of heterogeneous catalysts for biodiesel production. *Elsevier Journal*

55. U.S. Department of Energy. Office of Energy Efficiency and Renewable Energy. Freedom Car & Technologies Program. http://www1.eereenergy.gov/vehiclesandfuels/pdfs/basics/jtb_diesel_engine.pdf (accessed February 25, 2012).

56. Von Wedel, R. *Technical Handbook for Marine Biodiesel in Recreational Boats*; CytoCulture International, Inc.: Port Richmond, CA 1999. http://localenergy.org/pdfs/Document%20Library/Technical%20Handbook%20Marine%20Biodiesel.pdf (accessed February 25, 2012).

57. Santacesaria,E.; Pengmei, L.; Tesser, R.; Serio, M. Heterogeneous catalysts for biodiesel production*. Energy and Fuels* 2008, 22, 207-217.

58. Hanna,M.; Fangrui, M. Biodiesel production: a review 1. *Bioresource Technology* **1999**, 70, 1-15.

59. Fang,Z.; Guo,F. Wei, N.; Xiu,Z. Transesterfication mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Elsevier Journal* 2011, 08.064.

60. Ivashechkin, A, A.;et al. Biodiesel-Fuel: Content, Production, Producers, Contemporary Biotechnology (Review). Applied Biochemistry and Microbiology, 2010. 46. 4. 369-378