Alternative Liquid Fuels for Transportation

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ABSTRACT

This paper reviews present studies at F.I.T. intended to identify, evaluate, and develop alternative liquid fuels for transportation which can be derived from biomass using non-capital intensive processes.

INTRODUCTION

The energy supply problem asserts itself to the ordinary citizen in many ways:
1. Higher electric bills
2. Higher shipping costs
3. Less than dependable fuel supplies for transportation.

It is true that the days of long lines at gasoline stations seem to be over, and that gasoline prices seem to be stabilizing or decreasing. However, the International Energy Agency (IEA) estimates that the U.S. oil production will resume its historic decline by the end of the decade, and that world production will start declining in the mid 1990's. Lee Iacocca said in a recent issue of Psychology Today, "Once this recession induced oil glut ends, we'll be back in gas lines paying through the nose. This $1.25 gas we're enjoying is an aberration. It won't last long - a couple of years at the most." Thus much higher prices or lack of availability of gasoline will present problems to most of us in this room before long.

Hence, the world will soon be faced with difficult choices concerning alternative liquid fuels for transportation. The most likely alternative fuel to emerge will be synthetic liquids from coal or natural gas. However, these are all capital intensive processes requiring dedication of relatively scarce moneys of the Government and/or private industry which we can only hope will be available when necessary.

The most commonly proposed non-capital intensive liquid fuel for transportation is ethanol. 10% ethanol in gasoline is currently used as "gasohol" in the United States. Similar formulations are used in Brazil. Brazil also has a great deal of experience in the use of 95% ethanol as a fuel for automobiles. Ethanol, as everyone knows, can be and has been produced in large and small scale volumes since the dawn of history and perhaps, for that reason, it has received the most attention as a candidate alternative liquid fuel. However, ethanol may not be the best or only practical, non-capital intensive, alternative liquid fuel extender for gasoline. If not ethanol, what other fuels might be suitable?

ETHANOL

Ethanol is derived from microbial fermentation of glucose according to the following equation:

\[ C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \]

Ordinary commercial ethanol is a constant-boiling mixture of alcohol (95.57% by weight) and water (4.43%), and since this mixture boils at 78.2°, a temperature slightly lower than the boiling point of absolute ethanol, 78.3°, separation from water cannot be effected by ordinary distillation but it is prepared commercially by azeotropic distillation. When a mixture of 95% alcohol and benzene is distilled, the initial fraction consists of absolute alcohol. Only absolute alcohol is suitable for use in "gasohol". Fuel grade alcohol is also prepared by drying with zeolites.

Once obtained, the ethanol can only be used in 10-20% proportions in gasoline without carburetor or engine modifications. This is caused by the fact that ethanol is markedly dissimilar to gasoline as an auto fuel. The
fuel value of any candidate automobile fuel in a conventional unmodified gasoline engine is measured by determining the mass-air/mass-fuel ratio which is derived from the stoichiometry of the reaction with air.

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}
\]

As is seen, three moles of oxygen react with one mole of alcohol. The molecular weights of alcohol and oxygen are 46.07 and 32 respectively and thus the mass oxygen to fuel ratio is:

\[
\frac{3 \times 32}{46.07} = 2.08
\]

But since oxygen is 21% of the air the mass-air/mass-fuel ratio is:

\[
\frac{96 \times 4.76}{46.07} = 9.92
\]

If we proceed through the same exercises with iso-octane, an ideal automobile fuel, we see that the mass-air/mass-fuel ratio is 16.84. However, with ordinary regular leaded gasoline the ratio is generally about 14, since gasoline is a mixture. Thus, a conventional gasoline engine using pure ethanol will, theoretically, only be 59% as effective. In actuality, the engine will not run at all. In fact our experimental 1975 Pinto engine will hardly run at all on a 40% ethanol gasoline mixture. Only a 20% ethanol gasoline mixture performs adequately and thus for all practical purposes we are restricted to 10% ethanol-gasoline mixtures (as in "gasohol") unless we are willing to modify carburetors or engines. Once restricted to a 10% ethanol-gasoline mixture, a second problem arises - namely separation, phasing, or layering. If as little as 0.5% water should inadvertently be added to "gasohol" immediate separation will occur. This can easily happen when gasoline is obtained from leaky storage tanks. This action will not occur if the proportion of alcohol is 20% or higher, and, as we mentioned before, "gasohol" contains only 10% ethanol. Thus, we can see that there are serious problems with the use of ethanol as a gasoline extender. (See Table 1).

OTHER CANDIDATE ALTERNATIVE LIQUID FUELS

If ethanol is such a problem in a conventional unmodified gasoline engine, what are the alternatives? What is needed is a liquid fuel, readily derivable from biomass material, which is soluble in gasoline, and similar to gasoline in mass-air/mass-fuel value. One candidate item derivable from biomass is furfural. Furfural is produced commercially today from corn cobs and rice hulls. It is a yellowish liquid produced by acidification of the feedstock followed by distillation. However, there is one major problem. Furfural is not soluble in gasoline and hence cannot be considered as a gasoline extender. There is, however, a second problem - cost. As of January 3, 1983, the Chemical Reporter stated that furfural in tank cars sells at $0.66 a pound which is equivalent to $6.37 a gallon. At face value this seems like a truly non-competitive price - six times more expensive than gasoline or diesel fuel in the U.S.. However, the density of furfural is 1.156 as compared to ethanol (0.785) or gasoline (0.739). Thus, if we compare costs on the basis of weight instead of volume, there is only a differential factor of 3-4 involved since ethanol sells for $0.23/lb. and gasoline sells for $0.18/lb. in the U.S..

Therefore, in Europe, where gasoline is in the $3-5/gallon price range, furfural might be close to being competitive. Furfural, however, is not soluble in gasoline or diesel fuel and thus only a few researchers are currently investigating its use as a diesel fuel. (See Table 2).

Are there any further alternatives? There is levulinic acid (ref. 1). Levulinic acid can be derived by acid treatment of hexose sugars such as glucose or cellulose according to the following reaction:

\[
\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{acid, heat, pressure}} \text{CH}_3\text{CH}_2\text{CH}_2\text{C-OH} + \text{HCOOH} + \text{H}_2\text{O}
\]

Levulinic acid itself is not soluble in gasoline, but, levulinic acid can be converted by distillation at 150°C to gasoline soluble α-angelicalactone:

\[
\begin{align*}
\text{α-angelicalactone} & = \text{levulinic acid} \\
& \xrightarrow{\text{α-angelicalactone}} \text{levulinic acid}
\end{align*}
\]

It might seem at first glance that distillation at 150°C is a high energy process in comparison to ethanol which boils at 78°C when in fact it actually takes less energy to distill a gallon of angelicalactone than to distill a gallon of ethanol (see Table 3). Levulinic acid is a major product of the controlled degradation of hexose sugars by acids. Because the supply of hexoses from cellulose-containing plant material is immense and replenishable, conversion of such materials into a single chemical product.
meets one of the requirements for a fuel extender.

Although levulinic acid has been known since the 1870’s, when many of its reactions were first established, it has never reached commercial use in any significant volume.

Hexoses are convertible to levulinic acid by essentially a process of dehydration and cleavage of a mole of formic acid. The theoretical yield from a hexose is 64.5%, but the literature (ref. 1) shows that only about two thirds the theoretical yield can be attained; the balance proceeds to insoluble residues. Substantially the same yields from cellulose in Douglas fir sawdust were amply demonstrated. Formation of levulinic acid from low-cost cellulosic products overcomes one of the major difficulties encountered in other fuel extender production processes.

PROCESS DEVELOPMENT

Process development in the laboratories of MRI/FIT, is concerned with optimizing the process of conversion of glucose or cellulose to angelicalactone according to the following scheme.

\[
\text{glucose or cellulose} \xrightarrow{\text{acid, steam pressure}} \text{levulinic acid} \xrightarrow{\text{distillation at } 150^\circ} \text{angelicalactone}
\]

Angelicalactone is currently preferred over other possible fuels derived from levulinic acid since its production requires only one step. Angelicalactone dissolves in gasoline and 20-50% mixtures have been tested in our test stand engine and were found to be indistinguishable from gasoline in performance.

PRODUCTION OF ANGELICALACTONE FROM BIOMASS

The production of angelicalactone from biomass can be divided into four basic steps. These steps are: 1) production of crude levulinic acid, 2) extraction and purification of the levulinic acid, 3) conversion of levulinic acid to the crude angelica lactone, and 4) extraction and purification of the crude angelica lactone.

1. **Production of Crude Levulinic Acid**

The batch reactor used to produce the crude levulinic acid from the biomass can be an agitated pressure reactor or a simple autoclave reactor. The feed streams into the reactor are the biomass, the mineral acid (such as HCl or H₂SO₄), and two aqueous waste streams. The aqueous streams are used to dilute the mineral acid to an appropriate concentration. These streams are used instead of plain tap water because they contain trace amounts of our intermediate and final product. By using them to dilute the acid, product yields can be improved and waste water treatment can be reduced. The output stream of the reactor consists of the crude levulinic acid in an aqueous, acidic solution.

Laboratory experiments were performed to determine what materials would be suitable for the reactor vats. Trials performed in a small autoclave reactor showed that all grades of stainless steel would be unsatisfactory. This information narrowed the reactor material selection to either plastic or glass.

Reactions performed in a small autoclave showed encouraging results. A large autoclave was available at MRI/FIT and was brought to the plant site for installation. Glass tanks served as the reaction vessels for the autoclave. High density plastic (PVDF) served as the lids for the tanks since tests conducted using the small autoclave showed that PVDF plastic is compatible with the reagents at working temperatures and pressures. The approximate cost for the plastic lids and the glass tanks are $475. By using the autoclave rather than an agitated reactor, considerable capital was saved. Controls on the autoclave exist to monitor pressure, temperature, and time of reaction. The reactants and products can be pumped into or from the tanks before and after the reaction using a peristaltic pump and plastic tubing. A steam generator is, of course, necessary regardless of the choice of reactor. While this unit was being established, laboratory reactions continued using the small autoclave. Initial experiments were performed to see what cellulosic feedstocks gave the best levulinic acid yields under varying conditions. The results of sawdust and HCl experiments show that the maximum percentage yield of levulinic acid occurs at HCl concentrations of about 8%. The results also showed that the remaining dextrose or glucose in the samples decreases as the acid concentration increases. For 8% HCl, the maximum yield is 6.9% levulinic acid. All these reported yields are based on molar percentages.

Shredded paper was also used as the biomass feedstock. These results showed the maximum yield to be also at 8% HCl. However, this yield is at 17.2% as opposed to 6.9% using sawdust. Thus, the data indicates that yields from paper are higher than from sawdust in this process. It was also found that the dextrose concentrations decrease as the percentage of HCl increases.
Further experiments were performed to determine the optimum acid concentration which gives the highest percentage yield of levulinic acid. Experiments were conducted using 2, 4, 6, 8, 10, and 15 percent HCl. The results showed that for dextrose trials, the maximum levulinic acid yields occur at HCl concentrations between 7 and 15 percent. Another second experiment was set up to obtain the optimum values between these limits.

The results of this experiment show that the optimum acid percentage is found to be at about 10% HCl.

Knowing that the best yields result at HCl concentration of 10%, more experiments were conducted to see what the optimum dextrose concentrations were. In all of these trials, the amount and percentage of acid remained constant. It appears that the highest percentage yield of levulinic acid occurred at the lower dextrose concentrations. However, this result can be misleading, because the levulinic acid yields at high dextrose concentrations are only about 5% lower than those at low dextrose concentrations. When the costs of steam needed to run the reaction are considered, it may be cheaper to run at high dextrose concentrations to increase the volume of the product, since the percentage yield is not too different. Yields in the large autoclave may differ since it produces 50 to 75 lbs. steam per hour.

2. Extraction and Purification of Levulinic Acid

In order to purify and concentrate the levulinic acid produced in the first step of the process, a simple extraction or distillation operation can be used. The crude levulinic acid is first pumped through a solids separator, which may be a simple decanter or a gravity filtration device. Its purpose is to separate the solid residues produced in the autoclave reaction. The solids are disposed of or recycled while the liquids pass on to the next unit, the extraction tank.

The extraction tank can be a simple 50 gallon tank with an agitator. The crude levulinic acid is mixed with an appropriate solvent until equilibrium is established. The upper layer is then passed to the next unit, the solvent recovery system. The lower layer is washed with fresh solvent until the majority of the levulinic acid is extracted from the aqueous layer. All of the organics flow to the solvent recovery system while the aqueous wastes are discarded or recycled.

The solvent recovery system is some type of simple distillation assembly that separates the low boiling point solvent from the levulinic acid. This unit may be a rotary evaporator, a wiped-film evaporator, or any other efficient solvent recovery system. Once the solvent has been separated from the levulinic acid, it is recycled to the extraction tank to be used again. The residual levulinic acid then passes to the next step, production of the angelicalactone.

Various solvents are under investigation in the laboratory. Some of the more successful ones are dichloromethane, isopropyl ether, and methyl isobutyl Ketone. The optimum solvent would be one that is low boiling, has a high affinity for levulinic acid, and low cost. Also, concentration by distillation prior to extraction is being considered.

3. Conversion of Levulinic Acid to Angelicalactone

In this stage of the process, levulinic acid is dehydrated to the desired angelicalactone. The dehydration is carried out by a destructive distillation of the levulinic acid. This step only requires a distillation reactor and a steam generator for power. A sketch of the distillation reactor is shown on Figure 1.

The reactor includes a batch-wise still pot, a packed column, a condenser, and a decanter. A controlling system regulates and monitors the pressure and temperature in the batch kettle and controls the over-head column temperature. Levulinic acid is fed into the bottom still pot where the reaction takes place. An appropriate catalyst is either mixed with this feed stream or placed in the kettle. The products, angelicalactone and water, then pass through the column and condenser, where they then flow to the decanter. The decanter separates the organics and aqueous solutions. The organics (crude angelicalactone) return to the column to be purified while the aqueous liquid is used to dilute the mineral acid needed for the autoclave reactor. Since this aqueous layer contains approximately 10% angelicalactone its recycle enables better product yields: The lactone may also be extracted from the water if this process proves economically feasible.

When most of the water has been removed by the decanter, product angelicalactone is taken off by the reflux valve which is located between the decanter and column as shown on Figure 1.

Material testing in the laboratory indicates that 316 stainless steel is a compatible material for both reactants and product.

After several visits to inspect and discuss pilot plant units, a small 316 batch still was purchased as well as a 6.5 gallon kettle, a 3" packed column, and a five foot square condenser.
Steam requirements for the still range between 25 and 50 lbs. steam per hour. Totaling the power requirements of the autoclave reactor and the distillation reactor gives a requirement of 75 to 125 lbs. steam per hour. A steam boiler with two output steam lines was available which would allow one line at up to 100 lbs. per hour or two lines up to 50 lbs. steam per hour each.

The main goal of the initial lab experiments was to increase the product yield as well as limit residues and other undesirable by-products. Initial experiments were started using no catalyst and atmospheric pressures. The yields in these reactions ranged from 18.5% to 68.2%, but in all the reactions, a very gummy, viscous black residue remained in the still pot. This residue usually took two or three days of soaking in acetone to remove. Aqueous KOH as well as chromic acid cleaning solution had little effect on dissolving the residue.

Attention now shifted from achieving greater yields to removal of undesirable kettle residues. A nitrogen bubbler was placed in the reaction flask in hopes of lowering the rate of reactant oxidation and polymerization. Although this did not prevent the sticky residues the nitrogen helped carry product vapors through the column faster, thereby increasing product flow rates. It was decided to use a nitrogen blanket on all of the reactions performed in the lab.

The next area of investigation considered was the effect of catalysts on the reaction. Various dehydration catalysts were tried, including both dehydration catalysts and water abstracting reagents. The dehydration catalysts used were H3PO4, P2O5, and p-toluenesulfonic acid (p-TSA). The water abstracting reagents tried included Al2(SO4)3, CaCl2, and MgSO4.

All of the catalysts tried had a negligible effect, if any, on the molar percentage yield. However, one dehydration catalyst (p-TSA), and one water abstracting reagent (MgSO4) helped in the removal of the kettle residues. It seems that a one percent W/V solution of the catalyst to levulinic acid produces a final reaction residue that is a glassy, brittle, carbon-like material. This material is easily broken up to a powder and removed. Any remaining residue remaining in the still pot is emulsified by an overnight soaking in aqueous KOH. The material is now easily washed out after the KOH bath.

The next factor taken into consideration was the effect of temperature on the percentage yield. Angelicalactone exists in two isomers, α and 3. Lab results indicate that while higher temperatures increase the production rates, they also increase the percentage of 3-

angelicalactone in the product. The lower reaction temperatures produce more of the kinetically favored product, α-angelicalactone.

Much literature and laboratory work has been performed to develop and perfect analytical techniques used to quantify reaction results. Assays for α-, β-, angelicalactones, and levulinic acid, are performed on a high-performance liquid chromatograph. Other assays for sugars and moisture percentages have already been developed. More studies on catalysts, pressures and temperatures are currently underway. Modifications on the distillation reactor should help increase product yields and reduce residual materials.

4. Extraction and Purification of Angelicalactone

The final step in the process is the refinement and purification of the crude angelicalactone produced by the distillation reactor.

The angelicalactone extraction tank is similar to the levulinic extraction tank, except that a metered amount of base is added to the tank along with the organics and the solvent.

The base is used to neutralize any remaining levulinic acid that has not reacted but has passed through the distillation reactor. Bases such as Na2CO3 and K2CO3 have worked successfully in the lab.

Once the lactone has been sufficiently washed and extracted the aqueous layer of the extraction tank flows to a mixing tank where sufficient acid is added to change the levulinate back to levulinic acid. This solution is then used to help dilute the mineral acid used in the autoclave reactor. This recycle helps eliminate aqueous wastes and it helps improve product yields from the autoclave reactor.

The angelicalactone and organic solvent pass on to the solvent recovery system. This system is identical to that used to recover the solvent from the levulinic acid extractions. Here again the solvent is removed from the lactone and recycled back to the extraction tank. Solvents including isopropyl ether and dichloromethane have been successful, and more experiments are being done to test the feasibility and effectiveness of others. An optimum solvent here would be easily recovered and possess good anti-knock properties since trace solvent may remain in the angelicalactone.

The pure lactone is then immediately mixed with gasoline in a tank to produce a 60/40 mixture of gasoline/angelicalactone. This product is stored and saved for further dilution and engine testing.
FUTURE PROCESS DEVELOPMENT WORK

Future experiments are currently being conducted in the laboratory and in the pilot plant to optimize both yields and cost. A computer program has been prepared which allows immediate overall cost determination when any part of the process is changed. In particular, more small autoclave experiments are needed to determine optimum charge, reaction time, and temperature.

More extraction solvents must be tested to find the most suitable one although the solvents currently used work well. Also concentration prior to extraction must be explored. The cost effectiveness of the various angelicalactone refinement procedures is another area which needs attention.

Also, more data need to be compiled for the conversion or dehydration reaction. Much of this data is pending on the perfection of analytical techniques currently being developed.

COMPARATIVE MASS-AIR, MASS-FUEL RATIOS

This α-angelicalactone is perfectly soluble in gasoline in all proportions. The mass-air/mass-fuel values are 8.54. This value is quite a bit lower than that of ethanol and, thus, at first glance would not seem worthy of further consideration. However, the density of these angelicalactones is 36% higher than that of ethanol, and since the carburetor delivers a constant volume, 36% more mass of angelicalactone per unit volume is available for combustion than is the case of ethanol. (See Table 3).

Thus in order to obtain comparisons of the worth of various candidate fuels, the product of the multiplication of the mass-air/mass-fuel ratio and the density should be compared. If the candidate fuel is only a certain percentage of gasoline, the above named product should be multiplied by its fraction in gasoline. For example:

For 50/50 ethanol-gas mixtures

\[
(0.5)(9.94)(0.789) + (0.5)(14.5)(0.774) = 9.53
\]

For 50/50 angelicalactone-gas mixtures

\[
(0.5)(8.55)(1.084) + (0.5)(14.5)(0.774) = 10.25
\]

A summary of some comparative values is shown in Table 4.

It is readily seen that, at the 50% concentration level, angelicalactone has 91% of the fuel value of straight gasoline, but analogously ethanol has only 83%. So, at face value it would seem that angelicalactone is worthy of further consideration. Costs are somewhat harder to determine since levulinic acid is not a product which is sold commercially in great quantities. Current prices are in the range of $3.00/lb. which is mostly due to market considerations. Historically, however, levulinic acid has been prepared in one step from very cheap raw materials such as low-grade cellulose, glucose, and starch. These raw materials are similar to those used for the preparation of furfural and the processes are very similar to those used in preparing furfural. Therefore, it should be possible to prepare levulinic acid for a price equal to or below that of furfural and if envisioned improvements in the production process can be made, the price should be below that of ethanol and competitive with retail gas.

The fuel performance calculations actually reflect what happens with a conventional automobile engine. Actual test runs were conducted on a test stand 1975 Pinto engine as shown in Figure 2. This test stand engine is equipped with fuel uptake rate measuring device, a mechanical tachometer, and a brake horsepower meter. The data generated are converted to horsepower-seconds. The "seconds" is the time of uptake of 197.2 ml of fuel. When the mass-air/mass-fuel ratio is low, the horsepower-seconds obtained will be low. If the horsepower-seconds are too low the engine will "cough" or "run rough". As seen from the data in Figure 3, 30%, 40%, and 50% angelicalactone in gasoline is essentially equivalent to gasoline in performance whereas those concentrations of ethanol in gasoline result in poor performance. Hence, there seems to be some promise in angelicalactone as an alternative liquid fuel for transportation.

CONCLUSION

Simple low-energy chemical conversion of biomass to suitable liquids seems to be a reasonable non-capital intensive approach to gasoline extenders. Favorable analysis obtained from data generated by a pilot plant operation will be necessary to prove ultimate feasibility.

REFERENCES

TABLE 1

Effects of Water on Gasoline-Ethanol Solutions

<table>
<thead>
<tr>
<th>% (ml) GAS</th>
<th>% (ml) ETOH</th>
<th>% (ml) H₂O</th>
<th>Upper Layer (ml)</th>
<th>Lower Layer (ml)</th>
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<tbody>
<tr>
<td>94.5</td>
<td>5.0</td>
<td>0.5</td>
<td>99.5</td>
<td>0.5</td>
</tr>
<tr>
<td>89.5</td>
<td>10.0</td>
<td>0.5</td>
<td>98.5</td>
<td>1.5</td>
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<td>84.5</td>
<td>15.0</td>
<td>0.5</td>
<td>99.0</td>
<td>1.0</td>
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<td>79.5</td>
<td>20.0</td>
<td>0.5</td>
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</tr>
<tr>
<td>94.0</td>
<td>5.0</td>
<td>1.0</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>89.0</td>
<td>10.0</td>
<td>1.0</td>
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<td>84.0</td>
<td>15.0</td>
<td>1.0</td>
<td>94.0</td>
<td>6.0</td>
</tr>
<tr>
<td>79.0</td>
<td>20.0</td>
<td>1.0</td>
<td>NO SEPARATION</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2

Solubilities of Candidate Alternative Liquid Fuels in Gasoline and Diesel Fuel

<table>
<thead>
<tr>
<th>Candidate Fuel</th>
<th>Gasoline</th>
<th>Diesel Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Furfural</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>α-Angelicalactone</td>
<td>S</td>
<td>S 10%</td>
</tr>
<tr>
<td>Levulinic Acid</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>
## TABLE 3

Comparative Heats of Vaporization of Various Alternate Fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Mol. Wt.</th>
<th>( \Delta H_{\text{vap}} ) kcal/mole</th>
<th>Density</th>
<th>( \Delta H_{\text{vap}} ) kcal/gal.</th>
<th>Boiling Points °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>18.02</td>
<td>9.717</td>
<td>1.00</td>
<td>2,041.2</td>
<td>100.0</td>
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<tr>
<td>Methanol (CH₃OH)</td>
<td>32.05</td>
<td>8.43</td>
<td>0.79</td>
<td>783.6</td>
<td>64.5</td>
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<tr>
<td>Levulinic Acid</td>
<td>116.12</td>
<td>17.80</td>
<td>1.1447</td>
<td>664.0</td>
<td>246.0</td>
</tr>
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<td>Ethanol (CH₃CH₂OH)</td>
<td>46.07</td>
<td>9.22</td>
<td>0.79</td>
<td>601.9</td>
<td>78.5</td>
</tr>
<tr>
<td>( \alpha )-Angelica-lactone</td>
<td>98.10</td>
<td>12.22*</td>
<td>1.084</td>
<td>589.4</td>
<td>169.0</td>
</tr>
<tr>
<td>Furfural (C₅H₄O₂)</td>
<td>96.08</td>
<td>9.22</td>
<td>1.15</td>
<td>416.4</td>
<td>161.7</td>
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<tr>
<td>Tetrahydrofuran (C₄H₈O)</td>
<td>72.10</td>
<td>7.86</td>
<td>0.888</td>
<td>366.7</td>
<td>65.0</td>
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<tr>
<td>n-Hexane (C₆H₁₄)</td>
<td>86.17</td>
<td>6.90</td>
<td>0.66</td>
<td>200.0</td>
<td>69.0</td>
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<td>n-Octane (C₈H₁₈)</td>
<td>114.22</td>
<td>8.36</td>
<td>0.70</td>
<td>193.4</td>
<td>125.8</td>
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<tr>
<td>iso-Octane (C₈H₁₈)</td>
<td>114.23</td>
<td>7.82</td>
<td>0.69</td>
<td>179.4</td>
<td>99.0</td>
</tr>
</tbody>
</table>

* From Clausius - Clapeyron equation

## TABLE 4

Density - Mass-Air/Mass-Fuel Values of Various Percentages of Candidate Fuels in Gasoline

<table>
<thead>
<tr>
<th>% Additive in Gas (V/V)</th>
<th>100</th>
<th>50</th>
<th>40</th>
<th>30</th>
<th>20</th>
<th>10</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angelicalactone</td>
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<td>10.00</td>
<td>10.40</td>
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Figure 1. Distillation Reactor for Preparation of Angelicalactone
Figure 2. 1975 Pinto Test Stand Engine at F. I. T.
Figure 3. Experimental Performance Data for Various Gasoline Extenders