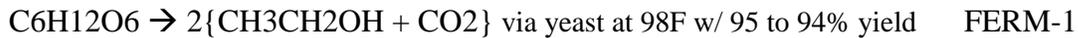


LACTIC ACID FUEL ROUTE

WHITE PAPER

A primary drawback to sugar fermentation to fuel grade ethanol is the 50% loss of carbon to CO₂.

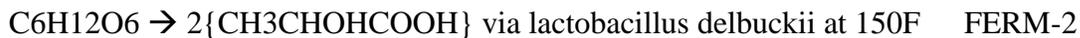


This side reaction is wasteful from both thermodynamic & carbon cycle view points.

This loss of carbon has various disadvantages such as:

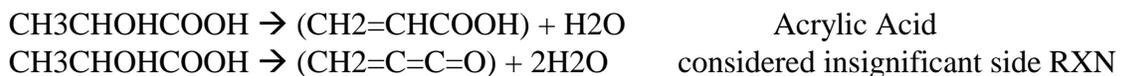
- Low grade heat production which produces CO₂ without performing useful work. Any recovery attempts such as heat pumps yield only marginal thermodynamic increases for process energy. Process thermal energy sources far better from a carbon cycle view point are: coal, bagasse, or fuel oil.
- The carbon from CO₂ returns back to the atmosphere without any useful work. This limits the potential carbon cycle benefits of the photosynthesis cycle of bio fuel production.

Hence this proposal for an alternative route via lactic acid from sugar. The basic reaction is:

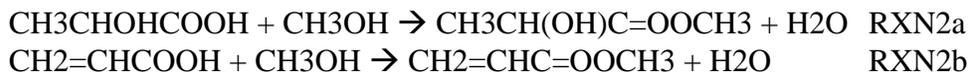


The reported yield is between 85% and 87% by weight. The fermentation is well documented and industrially accepted: RN Shreve, Chem. Process Industries. The lactic acid source could be from any likely carbohydrate source but most likely are sugar producing regions of South America. The problem is that lactic acid will not work as a fuel. Lactic Acid is known as a Hydroxy Acid due to the presence of both the hydroxyl group and the acid group. The presence of these groups should present opportunity for additional reactions to esters, ethers, or dehydration followed by dimerization.

A possible route would be treatment with sulfuric acid to yield a mixture of reactive compounds:



Treatment with sulfuric acid and MeOH to yield esters, Reaction 2



The formation of Allyl Alcohol (CH₂=CHCH₂OH) is considered insignificant via below routes:





Dehydration to ether compounds merits additional consideration. Ether compounds provide increased molecular weight for reduced vapor pressure while removing the acid radical. For example MTBE (MeOC(CH₃)₃) formed by MeOH and t-Butane has received wide acceptance as a fuel additive. However for lactic acid, the Ketone route is most likely route to higher MW compounds apart from the esterification reactions, ie MIK, MPK.

The methanol source for reaction 2 is remote source natural gas. Also the increased product mol weight obtained in reaction 2 is anticipated to minimize vapor losses over that of simple ethanol.

An important feature is the improvement of the carbon cycle over simple ethanol fermentation by using esterification. Two routes are proposed. Reaction A, (lactic acid/ethanol esterification), offers limited carbon cycle improvement. Reaction 2, (lactic acid/methanol esterification) provides auto fuel while expanding the resources of sugar producing regions. Reaction A, lactic acid/ethanol esterification, has only marginal increase in net yield $((.85*(90-18)+.94*46)/180)= 58.02\%$, as compared to 48% net yield for simple ethanol fermentation, $.94*2*46/180$.

Reaction 2 offers a $\{2*.85*(80-18)/180\}= 68.00\%$ overall weight yield on carbon when taking the water loss of reaction 2 against the biofeedstock. This is compared to a weight yield of 48.04% for ethanol alone. Thus reaction 2 offers a $68/48=142\%$ increase in yield over conventional fuel ethanol fermentation.

Some other considerations are:

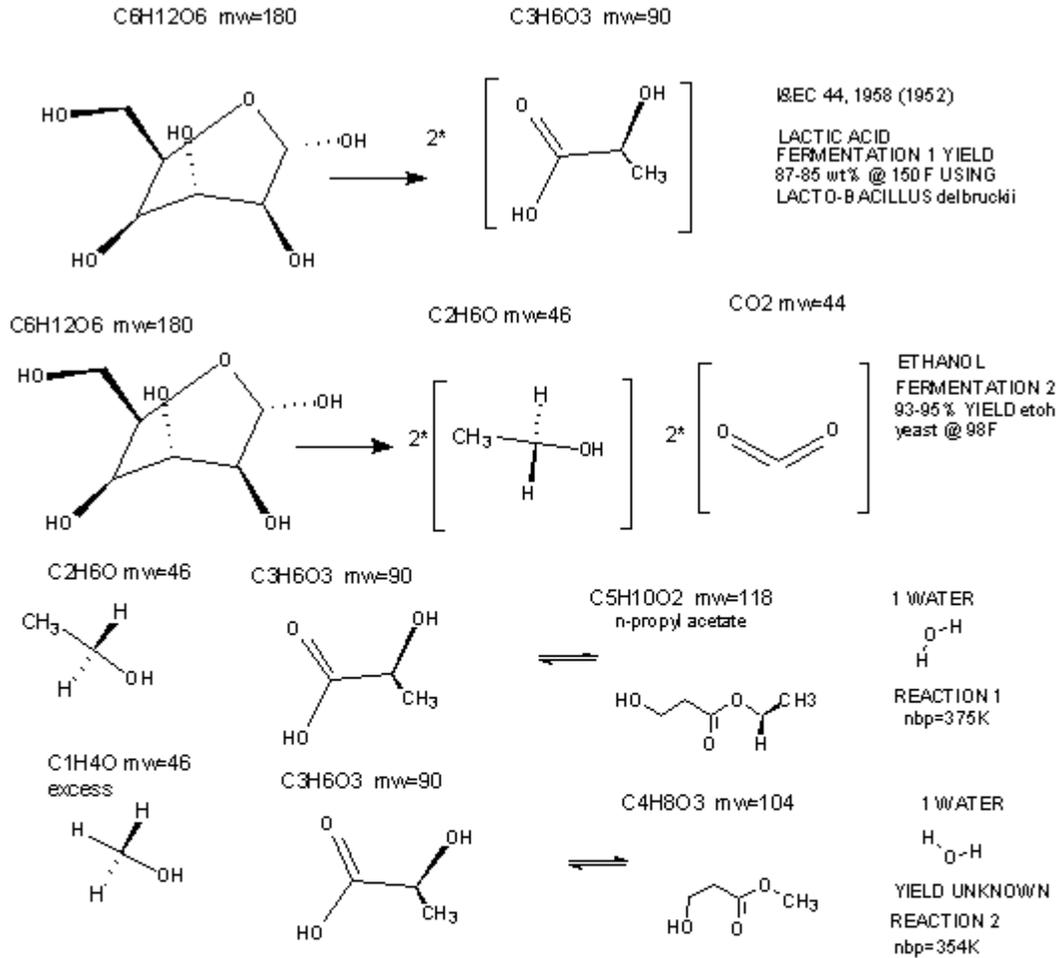
1. Sale by Volume, typical sales are by volume so the esterification route will offer less volume which must be taken into account as a deficit. However the positive aspects of the esters are well known from the MTBE program now widely used by refineries.
2. Increased octane properties (hence lower pollution which comes from the increased oxygen content) of esters compared to alcohols,
3. Increased fuel properties BTU/gal of esters as compared to alcohols, and
4. Reduced vapor losses of esters due to lower vapor pressures of esters compared to alcohols.
5. The extraction route may require more complex equipment due to the anticipated azeotropic distillation reaction and a possible extractive distillation to minimize Methanol loss and dewater the final product. For example, ethyl-acetate forms a 70.2C azeotrope of 82.15EtAc, 8.4%EtOH, 9%H₂O. This the water of the azeotrope would need to be extracted to make a suitable fuel product.
6. However after water extraction, a thermodynamic equilibrium between the products & reactants could limit the extent of water removal. Considering that the reaction requires catalyst & high temperatures, it is expected that kinetic factors can and will limit the reverse reaction & H₂O formation.
7. Storage in the presence of typical water levels is another consideration. For systems presently using ethanol fuel blends, these aspects will be marginal due to the

hydrophilic nature of ethanol fuel mixes. For conventional gasoline fuels systems, the water levels in storage tanks could have detrimental effects. Hence the nature of the reverse reactions merits some consideration.

8. Metallurgy, may be a consideration for facilities with carbon steel construction. The higher temperature & lower pH fermentation & distillation will present a more aggressive environment. Stainless steel & copper are typical materials selected for Et-Ac columns.
9. Availability of methanol supply for Reaction 2 is in competition for methanol used in the MTBE route. This is partially offset by the natural carbon ratio of butanes to methane in gas & oil fields. In the short run, methanol producers have an economic incentive to make only enough methanol for existing markets. A major methanol market is the MTBE product. Hence marginal costs for methanol production must command a premium to present market value of methanol to provide a production incentive. This fact is easily realized from recent increases in MeOH prices as MTBE production increased. The ultimate value is the BTU value when supplies become oversaturated. The recent run up in MeOH prices does not indicate an over saturation supply situation. Hence MeOH prices would be anticipated to increase if reaction 2 is commercially utilized on a large scale. In the long run reaction 2 becomes a win-win situation for both biomass producers & methanol producers, by minimizing impact of increased demand on oil producers and consumers.

Otis Armstrong.

Figure 1 LACTIC ACID FUEL ROUTE



The above reaction is only one possibility, other possibilities are DEG ($C_4H_{10}O_3$), n-Propyl-Formate, & Butanol series
 The favored reactions should be towards butanol series to minimize dehydrogenation which minimizes a acid consumption
 The basis for the above RXN is the classic ethyl-acetate reaction, modified to minimize steric factors & max fuel yield

