

# Ester Fuels and Chemicals from Biomass

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## Abstract

Bench-scale research demonstrated that using an efficient esterification step to integrate an ethanol with a carboxylic acid fermentation stream offers potential for producing valuable ester feedstocks and fuels. Polar organic acids from bacterial fermentations are difficult to extract and purify, but formation of the ammonium salts and their conversion to esters facilitates the purifications. An improved esterification procedure gave high yields of esters, and this method will lower the cost of ester production. Fuel characteristics have been determined for a number of ester-gasoline blends with promising results for lowering Reid vapor pressure and raising octane numbers.

**Index Entries:** Biorefinery; esters; esterification; alcohols; ammonium.

## Introduction

New opportunities for enhancing the value of agricultural products and improving their utilization require the development of innovative processes that are highly efficient, economically competitive, and environmentally acceptable. Potential applications in improved fiber and film technologies, safer biodegradable solvents, and less polluting oxygenate additives for fuels are ripe for commercialization, except that processing costs for the biobased esters that are the foundation of these applications are currently high. The development of refineries to conduct this processing of renewable resources will provide rural agricultural communities with an opportunity to diversify their economies and shift the dependence on petroleum-based chemical, polymer, and fuel markets.

## Dual Fermentation Biorefinery

The dual fermentation biorefinery (DFB) concept is a unique opportunity to integrate two types of fermentation: the well-developed yeast

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### Dual-Fermentation Biorefinery

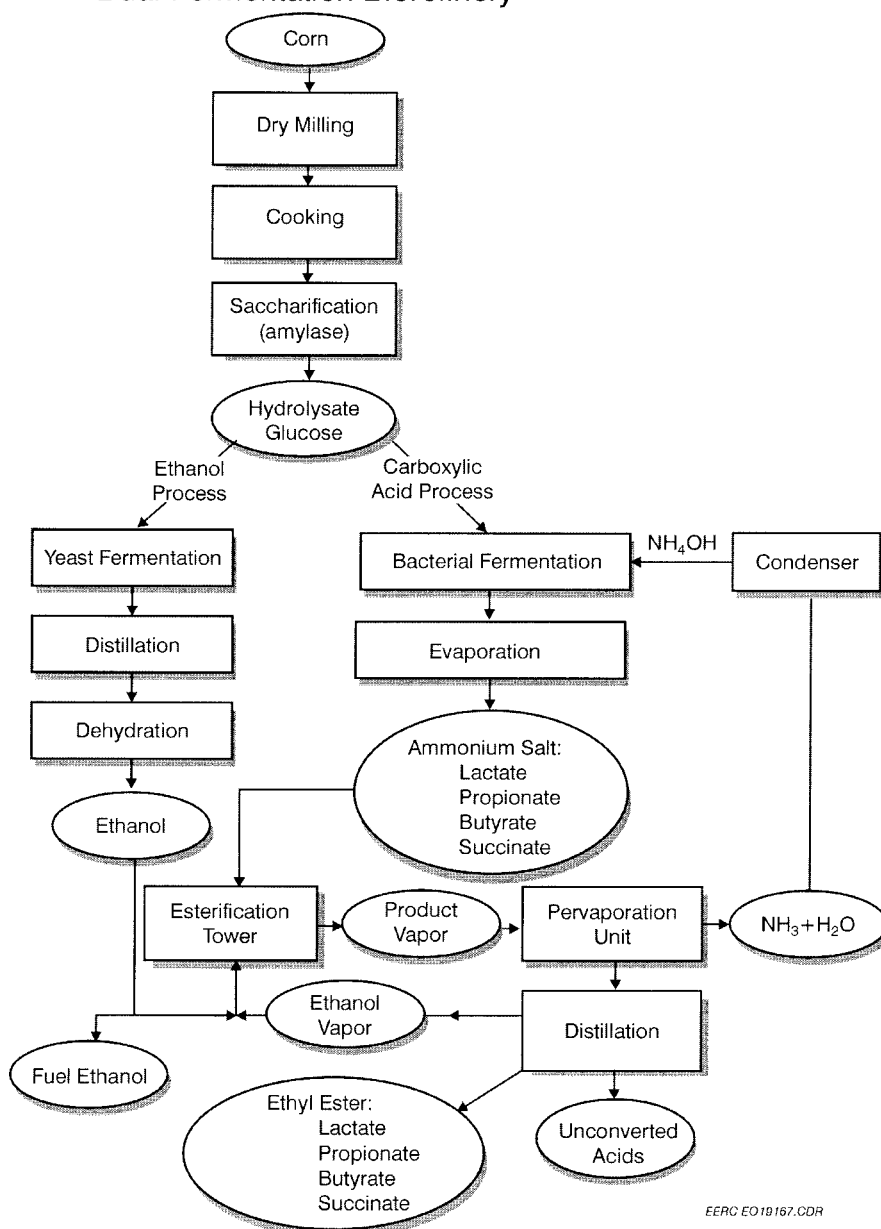


Fig. 1. Schematic representation of DFB.

fermentation of sugars to ethanol and the currently developing bacterial fermentation of sugars to organic acids. The DFB process, as illustrated in Fig. 1, produces high-value organic esters from these streams. The key to economic feasibility of the DFB is a high-yield esterification method that facilitates the isolation and purification of the organic carboxylate stream.

The fermentation of sugars to low molecular weight organic acids is well documented. Economical methods for extraction and purification of the acids, however, still present a challenge. Whereas ethanol is relatively easy to concentrate and purify owing to its volatility, the recovery of organic acids from fermentation is always problematic because of the high water solubility and high polarity of the acids. Thus, it is difficult to extract or distill some of these acids from the aqueous fermentation broth, and the cost of extraction and purification is significant for acids and derivatives prepared from them.

### Current Methods for Ester Production

In the traditional process in which calcium is used for neutralization during fermentation, the calcium salt of the organic acid product is acidified with  $\text{H}_2\text{SO}_4$ . Gypsum is therefore obtained as a byproduct. The acid form is extracted from the aqueous filtrate or concentrated by evaporation. For example, lactic acid is concentrated by multieffect evaporation to give the low-purity product. Heating the crude acid with ethanol and  $\text{H}_2\text{SO}_4$  catalyst gives ethyl lactate. The yield is equilibrium controlled, and it is difficult to remove the water and achieve higher than 60% yields. Improvements in the yields of purified lactate esters were demonstrated at the US Department of Agriculture (USDA) Eastern Regional Research Laboratory (1). This method passed methanol vapor (92–100°C) through the crude 82% lactic acid solution containing  $\text{H}_2\text{SO}_4$  catalyst or used a packed-column reactor tower with the methanol vapor. The condensate from the effluent vapors consisted of the ester, water, and excess methanol, which was distilled to recover the ester (80–90% yields) or hydrolyzed to obtain pure lactic acid (97% yield).

Cargill patents describe a concentration process for extracting lactic acid from the fermentation broth using a nonpolar tertiary amine after adjusting the pH with  $\text{CO}_2$  (2). The lactate is back-extracted from the amine phase. Owing to the high solubility in water, partitioning the lactate back and forth between phases requires very large amounts of solvent as well as back-extractant solution. The lactic acid is converted to the cyclic dimer (lactide), which is purified by vacuum distillation and subsequently polymerized in a melt process to polylactide, a biodegradable polyester resin with excellent fiber-forming properties. Related methods using ion-exchange columns for extraction have also been explored at the Energy and Environmental Research Center (EERC) and many other laboratories. Fouling of the resins is a major issue in these methods. Husson and King (3) reported a successful method for recovering lactate from a resin with tertiary amines.

An electrodialysis process was used at Argonne National Laboratories to concentrate lactic acid and regenerate base needed in the fermentation. The lactic acid is esterified with an ethanol in a patented pervaporation process that uses a membrane permeable to water and ammonia (4). The water and ammonia are removed from the separator cell by using a sweep

gas or vacuum and returned to the fermentation. The removal of water by the selective membrane thus drives the equilibrium and allows high yields of ester to form without extensive separation costs. The alcohol and product ester are separated by distillation. This process should be efficient, but there is concern that the membranes may foul with the large amount of impurities in the crude fermentation products. These potential fouling impurities include various biopolymers present, including reaction byproducts in the acid-catalyzed heated solution, such as Maillard and Browning reaction byproducts of the unfermented carbohydrates and proteins.

### **Direct Esterification in DFB Process**

In addition to providing diversified products for food, chemical, polymer, and fuel markets, the DFB concept is a unique opportunity for integrating recent and previous technical advances for processing carboxylic acids and their ester products. Purification of the acid fermentation products is needed and without esterification is very difficult. It is logical then to make the alcohol needed for esterification simultaneously as well as to market the purified ester products, rather than converting them back to acids.

A version of the DFB utilizing glucose hydrolysate is shown in Fig. 1. The glucose hydrolysate is divided into two streams: one for the conventional ethanol process and one for a bacterial fermentation to carboxylate salts. Ammonia is used for precise control of the pH, and thus the ammonium salt is produced. Multieffect evaporators concentrate the fermentation product salt by removal of water.

Esterification effectively couples the carboxylate fermentation stream (as a 70% aqueous solution of the ammonium carboxylate) with an ethanol distillate stream to form the desired ester directly in one step. This integration solves the carboxylic acid isolation problem without having to utilize the low-efficiency amine extraction and back-extraction process as described in the Cargill patents or other resin-based technologies that are subject to fouling problems.

Direct esterification of the ammonium salts is the key to effective processing of the organic acid stream. The problem is how to accomplish this step in high yields with methanol or ethanol. In flask experiments, Filachione and coworkers (5,6) demonstrated good yields in the esterification of ammonium salts with higher alcohols. The reaction of ammonium lactate with butyl alcohol gave 67% yields of ester, and higher alcohols gave higher yields. By recycling, an 83% yield of butyl lactate was obtained, and most of the ammonia was recovered. However, no esters were formed in reactions on ammonium carboxylates with lower alcohols.

The EERC direct esterification process used a modification of the published USDA method for acid substrates (1). In the EERC method, esters are formed in the specialized tubular flow reactor from the 70% ammonium salt concentrate and excess of alcohol and are removed in a vapor phase without the need for a pervaporation membrane as described in the Argonne patent (4) for preparing esters. The cost of membrane

replacement owing to fouling by the polymeric species in the concentrate is avoided. Initial bench-scale experiments gave ethyl lactate yields of 71%, based on ammonium lactate feed. This is an order of magnitude higher than those using the unmodified esterification tower.

In our initial studies, the entire overhead from the outlet condenser was collected in cold traps, and excess ethanol used in the esterifications was easily removed along with water and ammonia by distillation at atmospheric pressure, leaving a relatively pure ester product. Further work is needed to optimize this product separation and recover the ammonia for recycle to the fermentation unit.

The DFB process allows tremendous flexibility in producing a variety of products to optimize revenue through selective commodity production to satisfy changing market demands. The EERC direct esterification process is versatile and able to produce lactate esters for solvents and intermediates for high-value polylactide fibers or other esters for fuel additives, solvents, and chemical intermediates. The fermentable component(s) could be glucose derived from cornstarch as in most commercial ethanol plants in the United States, from sucrose from cane or beet sugars, or from sugars derived from other starches or lignocellulosic feedstocks. For example, DFBs could be established through the modification of existing beet sugar factories coupled with a new ethanol facility or the addition of a carboxylic acid plant to an existing ethanol plant.

The esterification process can also utilize other alcohols, such as inexpensive methanol produced from syngas. In this case, the process would not require ethanol fermentation, and the methyl ester would be produced from the organic acid fermentation product. Another option is to produce Guerbet alcohols (1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol) by catalytic condensation of methanol and fermentation ethanol.

## **Utilization of Ester**

Esters of the small organic acids resulting from the fermentation of sugars have the potential for use in many applications. A relatively small market is flavoring agents. For example, ethyl lactate is used as a flavoring for cheese. In addition, the esters offer great potential as biodegradable low-toxicity solvents, chemical intermediates for the preparation of polymers and plasticizers, intermediates for the preparation of pure forms of the corresponding acids, and fuel oxygenate additives. For the solvent and fuel additive alternatives in particular, the production cost would have to be substantially lower than the current values.

Ethyl lactate has been used for many years for solvent cleaning in the electronic industry. Wider application as a substitute for toxic hydrocarbon and halocarbon solvents in cleaning and degreasing; removal (stripping) of coatings, and manufacture of solvent-based paints, adhesives, and printing inks is being promoted. Ethyl or methyl lactate could be highly purified and then used to prepare polylactide, a biodegradable polymer with excellent fiber-forming properties. Plasticizers have been prepared by acylation of

lactate esters. The selling cost would have to be reduced from about \$2/lb to about \$1/lb for these applications to be commercialized.

## Performance of Ester Gasoline Blends

Oxygenate additives are needed for the efficient combustion and low emission properties of petroleum-based fuels. When added to gasoline, oxygenates such as methyl *tertiary*-butyl ether (MTBE) and ethanol provide octane and help reduce engine-out (prior to catalytic conversion) emissions of hydrocarbons and carbon monoxide. However, neither MTBE nor ethanol represents an ideal gasoline additive. Because of its presence and persistence as a contaminant in surface water and groundwater, MTBE has the potential to negatively impact drinking water supplies and is considered a human health hazard (7–9). Ethanol is not generally thought to represent a human health hazard, but when added to gasoline at concentrations of 2–15 vol%, it raises the Reid vapor pressure (Rvp) of the resulting blend by about 1.0–1.5 lb/in.<sup>2</sup> over that of the base gasoline. Ignoring this increase in Rvp, often referred to as the “ethanol bump,” results in increased evaporative emissions from ethanol-blended vs nonethanol-blended gasoline (10). Compensating for the ethanol bump requires removal and/or additional refining of high-volatility butanes to generate a reduced-Rvp base gasoline prior to ethanol addition, which adds to the consumer cost of gasoline. Ethanol is also miscible with water and has a higher affinity for water than gasoline, which can lead to ethanol separation from gasoline in the presence of water. Ethanol miscibility in water is the primary reason cited for disallowing shipment of ethanol-blended gasoline in pipelines.

As MTBE is phased out, first in California and later throughout the United States, the demand for clean octane will increase (11). Although ethanol could eventually meet this demand, an ideal octane supply would not require preblending volatility adjustment and would not preclude pipeline shipment of finished fuel. An even more ideal octane supply would effect an Rvp reduction on addition to a base gasoline, which would enable utilization of fuels with higher butane levels.

In 1982, Beuther and Kobylinski (12) evaluated a few esters for their potential as blending components of gasoline. They showed that both isopropyl acetate and an ethyl acetate/methyl acetate mixture provided good blending octane numbers that were comparable to alcohols and ethers but concluded that the cost of producing esters would keep them out of the oxygenate market. More recent studies at the EERC showed that ethyl acetate provided an increase in the  $(R + M)/2$  value in a 10% blend with gasoline, which was a little less than the increase observed for a 10% ethanol blend for this gasoline. This was accompanied by a decrease in Rvp of 0.6 compared to the 1.0 increase for ethanol.

To evaluate the stability of the fuel-additive blend in the presence of moisture, the extent of partitioning the additive from the fuel into a water phase was determined by shaking 50 mL of water with an equal volume of the fuel-additive blend. The volume increase for the aqueous phase was

Table 1  
Fuel Characteristics of 10% Oxygenate-Gasoline Blends

Fuel blend	Octane, (R+M)/2	Rvp (lb/in. <sup>2</sup> )	Oxygenate partition to water phase (%)
Base gasoline	86.9	13.2	—
10% Ethanol blend	89.4	14.2	100
10% Mixed alcohol blend	87.8	12.6	60
10% Mixed ester blend	88.3	12.4	0
10% Methyl propionate	88.7	12.4	0
10% Methyl butyrate	88.9	12.3	0
10% Ethyl acetate	<sup>a</sup>	<sup>a</sup>	20
10% Ethyl propionate	88.8	11.9	0
10% Ethyl butyrate	88.4	11.6	0

<sup>a</sup>Not tested with same base gasoline.

1.0 mL for the ethyl acetate blend, corresponding to 20% partitioning of ethyl acetate into the water phase. By contrast, ethanol partitioned 100% into the aqueous phase. Esters of longer chains should be expected to partition much less than 20% because of their lower water solubility. This would be a desirable fuel characteristic, since any partitioning may be unacceptable for fuel pipeline transport.

With the prospect of achieving a lower production cost for esters in the DFB process, a series of ester oxygenates was evaluated recently for use as gasoline octane providers. These oxygenates included esters made from fermentation-derived carboxylic acids (acetic, propionic, and butyric) in combination with methanol and ethanol. In addition, the acetate ester was prepared using a mixture of 3-, 4-, and 5-carbon alcohols derived from methanol and ethanol via an alcohol condensation reaction using a novel catalyst prepared at the EERC. The mixed ester was determined by gas chromatography to be composed of methyl acetate (1.3%), ethyl acetate (1.3%), *n*-propyl acetate (11.5%), isobutyl acetate (81.7%), 2-methyl-1-butyl acetate (1.2%), and other components (1.9%).

Each oxygenate was added to gasoline at a blend ratio of 10% and assessed for viability as a gasoline additive on the basis of octane as (RON + MON)/2, Rvp, and resistance to water contact-induced phase separation. Gasoline-additive blends were analyzed for Rvp, research octane number (RON), and motor octane number (MON) according to American Society for Testing and Materials Methods D5191, D2699, and D2700, respectively. The results are given in Table 1. For comparison, Table 1 also provides data for a 10% ethanol-blended gasoline, a blend of the alcohol mixture that was used in preparing the mixed esters, and the gasoline used as the base fuel for all the oxygenate blends.

All the esters exhibited good cold-weather blending characteristics. The blends all appeared as a clear solution and exhibited no phase separation at 1°F after standing for 1 wk.

The additive partitioning test results listed in Table 1 indicate excellent resistance to water-based phase separation. Although loss of ethyl acetate was previously determined to be 20%, loss of esters to the water phase was negligible for all of the ester blends with larger acyl components. The extent of aqueous-phase partitioning decreased as expected with increasing molecular size. The observed resistance to phase separation in the presence of water means that pipeline transport of gasoline containing these compounds may be possible.

The octane number test results (Table 1) indicated that the esters all provided a significant increase in the mean octane rating, with methyl butyrate achieving a 2.0 unit increase. The mixture of acetate esters gave the smallest increase. The octane test results are consistent with results reported in 1982 for several other esters (12). By comparison, the mixed alcohol blend showed a smaller increase in octane numbers than that observed for both the esters and ethanol blends.

The results listed in Table 1 show a beneficial depression in Rvp for the ester blends of 0.8–1.6 lb/in.<sup>2</sup>. As expected, the reduction Rvp of the ester blends varied inversely with molecular weight of the ester.

## Opportunities for Ester Fuel Biorefineries

Bench-scale research demonstrated that the DFB process with an efficient esterification step to integrate the fermentation streams offers potential for producing valuable ester feedstocks and fuels. The conversion of cornstarch to sugars is currently the most economically viable scenario, and the ethanol production operations are well defined; the economical production of the organic acids and esters, the key technical focus of the current research, still requires optimization and economic evaluation of the fermentation, evaporation, esterification, and product purification unit operations.

The fact that the esters provide Rvp reduction along with an octane boost could translate into an opportunity for oil refiners to reduce production costs associated with stripping butanes from gasoline. Currently, high-volatility butanes are removed from gasolines destined for sale in regions with volatility restrictions. Because of the Rvp reduction that the esters provide, the addition of ethyl propionate or ethyl butyrate to a gasoline could offset all or a portion of the gasoline volatility contributed by butanes, thereby reducing or eliminating the need for butane removal.

Although the Rvp of the inexpensive mixed alcohol blend was low, conversion of this mixture to the ester resulted in a greater enhancement of the octane numbers and provided a fuel with no loss to the aqueous phase. Thus, it is clear that greater benefits in oxygenate blending are possible with the esters, compared with higher alcohols.

This research as well as that reported earlier showed that esters are excellent fuel additives, providing high-octane blends and low volatilities. Emission characteristics are expected to be comparable to other oxygenate additives. While production costs have heretofore prohibited their use in fuels, DFB offers the opportunity to lower these costs.



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