

Final Technical Report

**Project Title:** Citrus Waste Biomass Program

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**Recipient:** Renewable Spirits LLC **DOE Award Number:** DE-FG36-04GO14331 **Covering Period**: 9/30/2004 – 9/30/2006

**Working Partners:** USDA Agricultural Research Service CRADA 58-3K95-4-1053 **Cost-Sharing Partners:** None **Project Director:** Scott Stevenson

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#### Executive Summary

Florida has 103 million citrus trees on 800,000 acres that last season provided 287 million boxes of citrus (80% of U.S. production); 85% went to Florida's 23 citrus processing plants. In juice processing one half of a citrus fruit is waste, yielding 5 million tons of wet waste, equating to 1.25 million tons of dry waste. Traditional use for these residues is as cattle feed which currently does not have sufficient value to cover the production/transportation costs. These materials are rich in pectin and other polysaccharides which can be hydrolyzed into sugars. This equates to a potential production of 120 million gallons of ethanol per year. Renewable Spirits LLC in collaboration with a CRADA partner, USDA/ARS Citrus and Subtropical Products Laboratory, developed an innovative process for the production of ethanol from citrus processing waste (CPW). The novel process based on enzymatic hydrolysis of CPW and fermentation of resulting sugars by yeasts was successively scaled up from laboratory scale to a 10,000 gal fermentor level. Numerous technical obstacles were overcome and continuous pretreatment and hydrolysis/fermentation sections were designed, constructed and successfully tested.

Preliminary economic evaluation indicates that the process is competitive with the production of fuel ethanol from corn and after a continuous distillation unit is constructed and tested, further scale up to a commercial level will be pursued.

# Project Description

1. Original Project Goals and Objectives

Project goal was to establish the technical and commercial viability of producing fuel ethanol and by-products from citrus processing waste. The objectives of R&D effort were as follows:

- Procure supply of citrus (i.e. orange and grapefruit) processing waste (CPW)
- Develop pretreatment methods to remove microbial inhibitor limonene and aid subsequent enzymatic hydrolysis and fermentation.
- Develop systems and methods for enzymatic hydrolysis of citrus processing waste and fermentation to ethanol.
- Develop yeasts and bacteria for this fermentation.
- Integrate production of ethanol from citrus waste into a single process.
- Scale up integrated process to pilot plant and commercial level.
- 2. Variance from original goals and objectives

None. The following subtasks were not completed by the end of contracting period:

- Fermentation of pretreated CPW with recombinant *E. coli* was not pursued.
- Continuous distillation of fermented CPW was not tested on pilot plant scale.
- Scale up to 75,000 gal level was postponed

These subtasks and commercial scale-up are being pursued at the present time.

## Discussion

1. Orange and Grapefruit Waste Feedstock Testing

CPW is a complex feedstock consisting of orange or grapefruit peel, segment membranes and small amounts of seeds, twigs and leaves. Orange or grapefruit waste is available either individually or commingled, depending on the processing plant and time of season. The CPW feedstocks were analyzed for soluble and insoluble carbohydrate composition, soluble and insoluble dry matter content and D-limonene content. The complex nature of CPW dictates use of a mixture of pectinase, cellulose and usually beta glucosidase enzymes for efficient hydrolysis of cell wall polysaccharides and their conversion to monomeric sugars. It must be noted that individual enzyme preparations are also mixtures of several enzymes which in concert hydrolyze particular cell wall polysaccharides. More potent pectinase preparations for example, contain not only several pectinolytic enzymes, but also additional hemicellulolytic enzymes which hydrolyze hemicelluloses of arabinan and galactan type. Since all these coupled hydrolytic activities are not measured or described by enzyme manufacturers, we tested several individual enzyme preparations from different manufacturers for efficacy of hydrolysis of CPW or its components. The enzymes were tested both individually and in mixtures because no single enzyme preparation could efficiently hydrolyze CPW. The enzyme mixtures were tested both in simple saccharification and in coupled simultaneous saccharification and fermentation (SSF) systems in order to test for compatibility of hydrolytic enzymes with yeasts. No problems were encountered in terms of toxicity of enzyme preparations towards yeast and 2-3 potent pectinase and cellulase preparations were identified which increased total sugar yields from about 23 to about 62% of the dry matter. However a large part of the enzymatically released sugars is galacturonic acid, arabinose, galactose and xylose. These sugars are either nonfermentable or weakly fermentable (galactose) by yeasts. Increase in sugars (glucose and fructose) which are

fermented by yeasts was relatively modest (about 25%), but fermentation of CPW without addition of enzymes proceeds very poorly and very low ethanol yields are obtained. The unhydrolyzed CPW is also difficult to pump and mix which affects pH and temperature controls and also distribution of biocatalysts. Despite claims of some manufacturers no cellulase preparation with sufficient beta-glucosidase activity has been identified and even SSF's have to be supplemented with beta glucosidase enzymes. The consumption of expensive enzymes was decreased several fold by pretreatment and a decrease in end product inhibition was observed by application of SSF approach. The cost of enzyme mixture was decreased from estimated \$10/gal of ethanol to 50-90 cents/gal ethanol through the course of the project. Important results were also obtained from investigations of enzymatic hydrolysis of grapefruit processing waste (GPW). It was found that this previously untested waste is as easy to hydrolyze as orange processing waste (OPW) and can be readily incorporated into ethanol production process. All analytical work and laboratory scale testing and development of enzyme mixtures were performed under Cooperative Research and Development Agreement (CRADA) at USDA Citrus and Subtropical Products Research Laboratory in Winter Haven, Florida.

#### 2. Pasteurization/sterilization testing

It was found during the preliminary phase of the project that limonene in CPW does not completely inhibit fermentation of soluble sugars by microorganisms. Fermentation of raw CPW by lactic acid producing bacteria became especially troublesome during storage at warmer temperatures (70-95°F), during extended enzymatic hydrolysis of raw CPW and after removal of limonene containing solids by centrifugation. By the time of grant award the process was modified by the addition of pasteurization step involving heating the CPW to 100-150°C by steam. Incorporation of this step into the overall process eliminated contamination by lactic acid bacteria from CPW. Overall the bacterial contamination was not a serious problem at 100 and 1,000 gal fermentor level, but it caused difficulties after the 10,000 gal fermentor system was placed in citrus processing plant. The problem was traced to contaminated water used for washing the equipment and extensive modifications of piping which introduced tees and other zones of low flow where CPW became contaminated with bacteria. Contaminated water problem can be readily solved by switching to potable water supply and piping is also being modified to streamline the flow and aid cleaning of the system.

#### 3. Heating/cooling of pre and post hydrolysis feedstock

The changes made in design of the process to remove limonene and pasteurize the CPW before enzymatic hydrolysis introduced very challenging problems of heating CPW to 100- 150°C and cooling rapidly to 35-45°C required by enzymes and microorganisms. The difficulties are caused by poor heat transfer properties of solid CPW. Novel approaches to heating CPW, stripping limonene and cooling pretreated CPW were developed. Details are described in 3 patent applications which have been filed on this novel process and its components. Proprietary equipment was designed and fabricated for each stage of the scaleup and the system was ultimately processing up to 7-8 tons of CPW per hour for up to 60 hours per week. Cooling equipment was also designed and installed for each scale of the

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saccharification/fermentation part of the process and employed when necessary. All three scales (100, 1,000 and 10,000 gal) of saccharification/fermentation equipment did not require much cooling after initial adjustment of temperature, but increased need for cooling is anticipated in the next, commercial stage of the process. Proper commercial heat exchangers were identified and one of them has been successfully tested with 10,000 gal fermentor.

#### 4. Limonene Removal and Fermentation Testing

A terpene D-limonene is a major (90-95%) component of citrus peel oil. A large part (about 50%) of citrus peel oil is removed as water/oil emulsion by specialized washing systems during extraction of the juice from fruit. This so called cold pressed peel oil is then recovered by centrifugation and marketed to food, fragrance and chemical industries. Another part (about 25%) of peel oil (so called stripper oil) is recovered from waste heat evaporators during production of citrus molasses from CPW. The remaining part of the peel oil is vented to the atmosphere from stacks of CPW dryers during production of citrus cattle feed. It can be estimated that 10-20 thousand tons of peel oil (limonene) are released to the atmosphere every year and contribute to VOC part of the air pollution. The loss of revenue for citrus industry from un-recovered limonene is about \$20-40 million/yr. It also has a high toxicity for microorganisms and helps to protect citrus fruit against microbial decay. It is concentrated in specialized groups of cells (oil glands) in flavedo, the outer, colored portion of citrus peel. These cells have to be ruptured by physical or chemical means and peel oil stripped to decrease limonene concentration from 0.7-1.5% in raw peel to less than 0.25 (preferably less than 0.15) percent prior to addition of microorganisms and fermentation.

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Hydrolytic enzymes do not appear to be inhibited by limonene. Since most published methods for limonene removal, such as solvent extraction, separation by flotation and steam stripping at high dilutions of CPW, were not compatible with our system for production of ethanol, we developed two new processes for removal of limonene from solid CPW. The first method involved enzymatic hydrolysis of raw peel followed by centrifugation of the hydrolysate. Limonene is almost insoluble in water and is absorbed in residual suspended solids. Centrifugation removes suspended solids with absorbed limonene as pelleted compressed sediment. Clarified sugar solution was then readily fermented to ethanol by yeast. The system was successfully tested on pilot (50-500 gal) scale using continuous flow centrifuge, but the approach was eventually abandoned due to enzyme cost, losses of sugar in pelleted solids and bacterial contamination. Alternate approach was developed in summer 2004 and has been used for all subsequent scale up effort. This approach involves a proprietary (patent pending) steam stripping method which removes limonene from a variety of CPW to 0.08-0.20% levels. The steaming process also pasteurizes CPW and pretreats it for subsequent saccharification and fermentation. Limonene containing vapors are condensed; limonene (stripper oil) is removed from aqueous phase by decantation and recovered. Approximately 90% of limonene in CPW is removed and recovered by this method and the remainder can be recovered during distillation of ethanol. Limonene sells in chemical markets for 50-90cents/lb and will provide a significant by-product credit. Inhibition of the yeast *Saccharomyces cerevisiae* by limonene has also been tested and results are being published. Numerous tests conducted on laboratory and pilot plant levels demonstrated that pretreated, de-oiled CPW is readily fermented by a yeast *S. cerevisiae*. However, fermentation times are rather long (48-72 hrs) which indicates that some other

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inhibitors may be present in CPW. *S. cerevisiae* is a standard yeast species used in fuel alcohol production. It has a high productivity and yield of ethanol and has a generally recognized as safe (GRAS) status issued by Food and Drug Administration. However this and all other yeasts cannot ferment galacturonic acid to ethanol and like most other yeasts cannot ferment five carbon sugars, arabinose, and xylose, to ethanol. It can ferment galactose, but slowly and after considerable delay. A large part (about 40%) of sugars released by enzymatic hydrolysis is thus not utilized for ethanol production by this yeast and unused sugars have to be used in cattle feed or other products. Prior collaborative research between USDA and University of Florida led to a discovery that recombinant bacterium *E. coli* KO11 can ferment galacturonic acid to equimolar mixture of acetic acid and ethanol plus carbon dioxide. This bacterial construct can also ferment other sugars in CPW hydrolysates to ethanol and achieve much higher (60-80%) yields of ethanol than yeasts. Experiments using this recombinant bacterium for fermentation of hydrolysed CPW were contemplated for this project, but had to be postponed due to the following issues. The ownership of the licenses for this patented strain changed and the current owner has been reluctant to sublicense the strain. In addition the citrus processing industry expressed opposition to having any recombinant microorganism utilized in their plants and last but not least the recombinant *E. coli* is not compatible with commercial hydrolytic enzymes in optimal pH values. The SSF approach could thus not be used without development of new enzymes for CPW hydrolysis. If these issues can be resolved, future experiments using *E. coli* KO11 will be conducted. Testing and development of other yeast strains is contemplated as well.

#### 5. 1,000 and 10,000 Gal batch systems design and fabrication

Once a decision had been made in the summer of 2004, to proceed with the steam pasteurization, steam oil stripping and simultaneous saccharification and fermentation system (Fig. 1;) the design, procurement and installation of equipment commenced in September 2004 at the USDA Citrus and Subtropical Products Laboratory in Winter Haven, FL for the 100 gal batch fermentor system. The installation was completed in January 2005, and the system was operated and tested in 1st quarter of 2005. Since the operation and testing (described below) were successful, a scale-up to 1,000 gal batch fermentor was initiated in the same quarter. Larger equipment was designed, procured and installed at USDA Citrus and Subtropical Products Research Laboratory in spring of 2005. It was successfully operated and tested before the end of orange harvesting season (June 2005). This part of the project was thus completed one year ahead of schedule and decision was made to design a continuous process at 10,000 gal scale, using the 1,000 gal fermentor as a back up. A new system for continuous cooling of pasteurized, stripped CPW was developed (patent application pending) and successfully tested in summer 2005. The scale-up to 10,000 gal level necessitated move to a citrus processing plant because equipment became too large for space available at USDA Citrus and Subtropical Products Laboratory. Supply and handling of feedstock (CPW) was also becoming a problem because the 10,000 gal fermentor requires approximately 35 tons of CPW for a single experimental run. Negotiations with a citrus processing company were successful and design, fabrication and procurement of equipment for 10,000 gal fermentor system were initiated in fall 2005.The 1,000 gal fermentor was moved to a new location as well. Location of a new pilot plant inside an operating citrus

processing plant provided numerous design challenges due to space limitations, routing of utilities, coupling of pilot plant system with existing citrus processing lines and treatment of pilot plant residues in feed mill and other waste treatment operations. All these challenges were successfully overcome and operation of this large pilot plant commenced in January 2006. However, the completion of the whole system was delayed by about three months due to delays in fabrication of unique pieces of equipment for the pilot plant and late delivery of the 10,000 gal fermentor. The pilot plant equipment was instrumented with temperature, pressure and flow sensors and the system was wired for computer control. The software and PC were procured, installed by a skilled consultant and the pilot plant was successfully controlled by personal computer for the whole testing period. The only equipment which has not been procured and installed yet is a continuous distillation system because it is too costly for the current budget. However, a small batch still was fabricated and installed at USDA Citrus and Subtropical Products Laboratory. It can distill about 30 gal of fermented CPW to more than 100 proof ethanol and has been successfully used for that purpose. In addition a large batch still was designed, fabricated and installed at the citrus processing plant. It was successfully used to strip ethanol from 1,000 gal and 10,000 gal fermentation runs. However it cannot produce concentrated alcohol stream, because it does not contain rectification columns.

### 6. 1,000 and 10,000 gal batch system testing and optimization

A lot of optimization and testing of pretreatment, limonene removal, enzymatic hydrolysis and simultaneous saccharification and fermentation was carried out in 2004 and the spring of

2005 on 100 gal scale under tasks 1-4. Laboratory testing and development under these tasks also continued until the end of the project. As discussed under task 5, the 1,000 gal pretreatment and fermentation system was designed, fabricated and installed by spring of 2005 and tested with orange processing waste (OPW) until the end of the season (June 2005). The experimental runs were successful and 4.0-4.5% alcohol solutions were obtained. Main problems encountered were poor mixing in 1,000 gal fermentor due to undersized motor for the mixer and spoilage of the OPW upon storage at 70-80°F overnight. Batch cooling of OPW in tanks was also quite inefficient, but the problem was solved by design and fabrication of a novel continuous cooler. Optimization done in conjunction with laboratory tests, concentrated on decreases in enzyme and yeast loading. Experimental tests showed that by application of pretreatment and simultaneous saccharification and fermentation the cellulase and ß-glucosidase loadings could be decreased by almost two orders of magnitude and pectinase loading could be decreased as well. In practical terms the cost of purchased enzymes decreased from about \$10/gal of ethanol for separate saccharification and fermentation of untreated peel to 50-90 cents/gal for SSF of pretreated peel. Since significant decreases in enzyme prices are projected by manufacturers, this component of ethanol production cost should decrease even more in the future. Optimization of yeast loading was carried out and an order of magnitude reduction in yeast consumption was achieved. The cost of yeast cells thus became a minor issue. In conjunction with these studies a novel strain of thermotolerant yeast was tested for suitability in SSF of CPW and promising results were obtained. Application of such yeasts could decrease cooling costs.

Successful results from the 1,000 gal scale led to design, fabrication and installation of the 10,000 gal fermentor system in citrus (grapefruit) processing plant with the 1,000 gal fermentor becoming a secondary system. Emphasis was placed on continuous operation of the pretreatment part of the process and recovery of valuable grapefruit peel oil. The initial runs using the 1,000 gal fermentor were successful and 2.5-3.5% alcohol solution (beer) was obtained. The lower concentrations of ethanol obtained from grapefruit processing waste were caused by lower sugar content of grapefruit peel and dilution of GPW with water. Water was added to aid pumping the peel across the building and decrease load on the pump motor. Addition of water was dictated by the nature of the site and will not be necessary in commercial operation. The 1,000 gal fermentor system was later on connected to 10,000 gal fermentor and piping was extensively modified to accommodate additional connections and recycle loops. These modifications led to difficulties with sanitation treatments and accumulation of old CPW in parts of the system. Old CPW and dirty process water accidentally used for washing the fermentors and parts of the piping led to contamination problems with lactic acid bacteria which have not been satisfactorily solved until the end of the project. The water supply was changed to potable water, but the piping was not changed on time. Additional important modifications which were tested at 10,000 gal level were heat exchangers for cooling of fementors, condensation of limonene containing vapors and preheating of beer before batch distillation. The 1,000 gal fermentor was successfully cooled by water circulated in a fermentor jacket, but the 10,000 gal fermentor required a separate heat exchanger. A heat exchanger for viscous liquids was selected, procured and successfully tested. Tests revealed that pretreated CPW has to be macerated by a short enzymatic hydrolysis before it can be circulated through the heat exchanger unit. Preheating of

fermented CPW by indirect heat exchanger before batch distillation also proceeded without major problems as did stripping of alcohol in a batch still. However we did not have an opportunity to test the long term (weeks or months) fouling of heat exchanger equipment. Continuous limonene removal and recovery were also tested during this phase of the project and a combination of vapor separator, condenser (heat exchanger) and oil-water separator was run for days at a time during  $1<sup>st</sup>$  quarter of 2006. Collected stripper oil is stored at low temperature for testing and marketing purposes.

### 7. Waste Management Testing and Optimization

Waste management did not become an issue until the 10,000 gal fermentor level was reached. Integration with the citrus processor's waste treatment was initiated at that point. Pretreated but unfermented GPW was blended with other GPW from the plant and transported to local ranchers as cattle feed. GPW was not dried during last season due to high price of natural gas and low price for dried GPW. Fermented GPW and beer still bottoms were also blended with the rest of GPW from the plant and taken to cattle pastures. No ill effects from this material were reported by cattle ranchers. One 10,000 gal batch of fermented distilled GPW was taken by another processor and tested as an additive when their CPW was run through a dewatering process. No serious problems were encountered during pressing of CPW and GPW stillage blends. The shutdown of dried cattle feed production at our citrus processing facility precluded testing of complete integration between ethanol production and cattle feed mill part of the plant.

#### 8. 75,000 gal fermentation and distillation test

The scale-up of ethanol production process was terminated at 10,000 gal level due to insufficient funds for additional equipment and changes in ownership of cogeneration plant where larger fermentor and distillation equipment were located. Scale-up to this level is anticipated once new partnerships are formed and additional funds secured.

### 9. Production partnership with citrus processor

On site production facility in a citrus processing plant is now partially operational and addition of equipment for continuous distillation is anticipated. Discussions with citrus processors and other interested parties about scale-up to commercial size are in progress.

#### 10. Conclusions and Recommendations for Future Work

Two approaches for conversion of CPW to ethanol have been investigated. One involved enzymatic hydrolysis of CPW, followed by centrifugation to remove residual insoluble matter with limonene and fermentation of sugars in clarified supernatant. The second approach involved thermal pretreatment of CPW, followed by stripping of limonene, cooling and by stripping of limonene, cooling and simultaneous saccharification and fermentation of pretreated CPW using enzymes and yeasts in the same vessel. Despite greater complexity, the second approach is more attractive than the first one from a technical and economical point of view. The CPW is pasteurized during pretreatment, limonene is successfully removed and recovered from the vapor phase of the cooling stage and large savings in

enzyme consumption and cost are realized. Additional savings will be realized when the price for commercial enzymes is decreased by improvements and expansion of the ethanol producing industry. The process was successfully scaled up to 10,000 gal fermentor level and continuous pretreatment was accomplished. However attention has to be paid to sanitation of cooled CPW stream and fermentor itself, because contamination with lactic acid bacteria was relatively common occurrence at the 10,000 gal level. Utilization of pretreated CPW and stillage in cattle feed has been demonstrated but additional experiments are needed to ascertain compatibility of stillage with presses and driers in production of dried cattle feed within the citrus processing plant. It is anticipated that incorporation of stillage into dried cattle feed will be investigated during the current season. Overall it can be concluded that pretreatment and fermentation parts were successfully designed, constructed and operated. They are ready for additional scale-up, possibly to a commercial level. The only part of the process which has not been investigated is continuous distillation of saccharified and fermented CPW. This part of the process requires rather large and expensive distillation equipment and has not been pursued due to lack of funds. The distillation of fermented CPW was however tested in batch stills and no major problems were encountered. Due to importance of this part of the process it is anticipated that continuous distillation will receive a high priority during the next phase of the project. A preliminary estimate of production costs has been prepared and compared to production costs from corn in Table 1. The results show that production of fuel ethanol from CPW is attractive from economic point of view and competitive with production of ethanol from corn. Two areas which need to be targeted in future R&D efforts are enzyme costs and energy consumption. Another aspect of the project which did not receive attention was fermentation of hydrolyzed CPW with

recombinant of *E. coli* KO11. This fermentation could utilize more sugars in hydrolyzed CPW and significantly increase ethanol yield. Additional testing of this microorganism was postponed due to negative feedback from citrus processors. Most of the dried citrus feed is exported to EU and processors have to certify that this feed does not contain any genetically modified microorganisms (GMO). It is natural that under current circumstances citrus processors do not desire any GMO in their facilities. However, the approach has not been abandoned and fermentation hydrolyzed CPW will be tested next year on laboratory scale using *E. coli* KO11. Additional income can be derived from sale of byproducts such as pectin or its derivatives, flavonoids and waxes. Development of these byproducts is being pursued at USDA Citrus and Subtropical Products Laboratory and will be coupled to ethanol production as opportunities arise.



# Table 1. Production Costs (Cents/Gallon Ethanol)

#### Appendix D. Energy Savings

 The attraction of reducing our dependence on foreign oil for balance of trade, military and fuel security reasons is well documented. Specific to the ethanol production industry, the envisaged bio-refinery will contribute to improving energy efficiency and the economics of biomass technology by reducing ethanol prices regionally and consequently providing a viable alternative renewable fuel and a regional MTBE octane enhancer replacement.

 An energy balance comparison for corn, forest material and woody residue, urban waste and citrus waste is given below. A gasoline reference comparison is also given.

#### **Feedstock comparison of Energy Balance (in Btu/Gallon) for Ethanol Production plus a**



# **Gasoline Reference**

 Note: While there may be combustible residues with all biomass feedstocks, only in the case of the wood based feedstock, has it been included in the energy consumption of the combined ethanol plant and electricity generation plant. This was done on the assumption

that co-generation is fundamental to a wood based feedstocks success while it is not critical to the current corn or proposed citrus waste feedstocks. Therefore the Ethanol/Electricity Plant energy shows a net production of energy equal to 30,880 Btu/gal for wood based feedstock.

 While it is assumed that the California Energy Commission has empirical data to support the above analysis; that is not the case for the Citrus Waste feedstock. The data uses the following assumptions:

- 1. Energy for fertilizer and feedstock handling in the form of growing and harvesting, have been set to zero; as these energies are the burden of the primary juice products.
- 2. A nominal number of 100 Btu/gal is used for feedstock transport. The transport energy burden of getting the citrus to the processing facility is being carried by the primary juice product, just as feedstock transport for urban waste and forest residue is not incremental as a result of the ethanol production. The transport of the citrus waste from the citrus processing plant is within a 10 mile radius.
- 3. The 25,000 Btu/gal allocated to the ethanol plant is based on the assumption that 30% of the energy used, when compared with a typical corn to ethanol plant, would be saved by not having a pre-treatment (cooking) process.
- 4. A nominal number of 8,700 Btu/gal (50% of corn number) is used for allocation to the limonene and cattle feed co-products. This is largely an unknown at this time and cattle feed studies need to be done.

 Using the assumptions above shows a 17% improvement in net energy for citrus waste over corn feedstock. However, the primary goal is to displace gasoline, and with a net energy advantage of 93,770 Btu/gal, the worldwide opportunity (approximately 30% Florida, 30%

Brazil and 40% rest of the world) is to produce 400 million gallons of citrus waste based ethanol for a net energy saving of 37 billion Btu.

