Developments in Ethanol Production from Citrus Peel Waste

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The Florida citrus juice industry produces about 3.5 to 5.0 million tons of wet peel waste annually. This material currently is dried and sold, often at a loss, as cattle feed to dispose of the waste residue. Profitability could be greatly improved if higher value products could be developed and produced from the peel waste. In this paper, the development of a new process to make ethanol along with improved recovery of D-limonene from citrus peel waste is discussed. The process consists of four parts: pretreatment to remove and recover D-limonene, simultaneous saccharification and fermentation (SSF) to produce ethanol, distillation to remove the ethanol and treatment of the residue for use as cattle feed or other co-products. Pilot plant studies have demonstrated that citrus processing waste can be fermented to produce ethanol (approximately 4% w/v) with D-limonene obtained as co-product. In order to design an efficient and cost-effective distillation column to strip off ethanol, the heat transfer coefficient and specific heat of fermented citrus processing waste was measured under forced convection using a heat exchanger. The technical difficulties of stripping off ethanol from fermented peels are also discussed. This new technology provides an alternative disposal of citrus peel waste in the citrus industry.

Over the past 20 years, the production of fuel ethanol from agricultural waste has been studied extensively (Aden et al., 2002; Grohmann et al., 1992, 1994, 1995, 1998; Wooley et al., 1999). Although much progress has been made, high production costs remain the major obstacle to commercial production of fuel ethanol from agricultural waste, such as wheat straw, sugarcane bagasse and corn stover (McAloon et al., 2000; Mielenz, 1997). A novel process, developed by USDA/ARS scientists and their partner Renewable Spirits, LLC has made significant progress in overcoming this economic obstacle. In this process, D-limonene, a high value co-product, is also recovered from citrus processing waste (CPW), thereby lowering the production cost. The production cost of citrus ethanol was estimated to be approximately $1.23/gal (Zhou et al., 2007), lower than the cellulosic ethanol ($1.35–1.62/gal) (Eggeman et al., 2005). This new technology has given rise to the potential of commercial ethanol production from CPW.

CPW is comprised of peel, rag (segment membranes and cores), juice sacs, and seeds. The major components of wet CPW are approximately 80% water, 6% soluble sugars, 5% cellulose and hemicellulose, 4% pectin, and 0.8% limonene (Grohman et al., 1995). While significant progress has been made in developing the process, several technical difficulties must be overcome before commercial production of citrus ethanol becomes a reality.

In order to make the process more economical, enzyme requirements have been optimized, resulting in extremely viscous pectin residues in the fermented CPW. Distilling viscous material is difficult and needs to be demonstrated. It is well-known that the efficiency of a distillation column is inversely proportional to the viscosity of distillation feed (Aden et al., 2002; Wooley et al., 1999). Therefore, in order to lower production costs, additional pretreatments to lower viscosity, along with minimal amounts of enzymes in the SSF process may be necessary for distillation to be operated efficiently.

In addition, distillation of fermented CPW involves heating and cooling under convective flow conditions. Knowledge of the heat transfer coefficient (h) is fundamental to the design, modeling, and optimization of a distillation process. Theoretically, the heat transfer coefficient (h) can be predicted using a model based on the flow characteristics of processed materials and their physical properties, such as viscosity, specific heat (C_p), thermal conductivity (k), and diffusivity (α) (Datta, 1999). However, due to the complexity of processed materials and flow characteristics, the prediction could be inaccurate. In practice, the heat transfer coefficient needs to be measured experimentally under similar flow conditions to the actual process.

In this paper, a new process (patent pending) is described and technical aspects are discussed. The physical properties of fermented CPW, such as viscosity, specific heat and heat transfer coefficient, were measured and the results presented. This paper provides data and guidelines for engineering design and feasibility study of commercial ethanol production from CPW.

Materials and Methods

MATERIALS. Fresh CPW ('Valencia' orange) was obtained from a local citrus processing plant. The density of wet citrus peel is 1030 Kg/m³ at 23 °C. Pectinase, cellulase, and β-glucosidase were purchased from Novozymes, Inc., Franklinton, NC. Calcium

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carbonate (99+%) was purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI).

In this paper, we studied the first three parts of the process for making ethanol from CPW. They are: pretreatment, SSF (hydrolysis and fermentation), and distillation (see Fig. 1). The fourth part of the process was beyond the scope of this study.

Pretreatment. In a pilot plant study, CPW (30–40 gal) were heated to above 150 °C (70 psi) by injecting high pressure steam. The pressurized CPW was then transfered into a flash tank with a sudden release of the high pressure to atmospheric. This caused the steam and limonene to be flashed off from the CPW. The effluent was cooled by a condenser, and collected in a separation tank. The resulting condensates were allowed to stand over night, during which time limonene separated from the aqueous phase. The pretreated CPW was collected in a 50-gal tank and cooled down to 38 °C for subsequent SSF.

Simultaneous saccharification and fermentation (SSF). With continuous agitation, appropriate amounts of calcium carbonate, cellulase, pectinase, glucosidase and *Saccharomyces cerevisiae* yeast were added to the pretreated CPW, and the agitation was continued for 2–4 h to ensure proper mixing. The CPW was then allowed to hydrolyze and ferment simultaneously at approximate pH of 4.2–4.8 for 48 h with occasional mixing until all the cellulose was digested and the resulting sugars were completely converted into ethanol. The ethanol yield was determined by HPLC (Pecina et al., 1984). The residual solid content was determined by drying an aliquot of the fermented mash in water to a constant weight at 70 °C (Grohmann et al., 1995). The fermented peel contained 4% to 5% ethanol by volume and about 10 wt% solids.

Physical properties of fermented CPW. Flow characteristics of the CPW, which influence the heat transfer coefficient, largely depend on viscosity. In this study, viscosity was measured using a Thomas–Stormer viscometer (Thomas Scientific Co., Swedesboro, NJ). The heat transfer coefficient (h) and specific heat (C_p) were measured using a custom made heat exchanger. Thermal conductivity (k) and diffusivity (α) values were estimated using a linear regression model with data in the literature (Charm, 1971).

Distillation. After SSF, the resulting mash was charged into a batch distillation unit to strip off ethanol. Distillation involves heating and cooling fermented CPW under convective flow conditions. Based on the measurements and estimates of fermented CPW, a pilot scale distillation tower was designed and is being installed in the USDA lab in Winter Haven.

Results and Discussion

The process consists of four parts: pretreatment to remove and recover D-limonene, simultaneous saccharification and fermentation (SSF) to produce ethanol, distillation to remove the ethanol and treatment of the residue for use as cattle feed or other co-products. In order to dispose the stillage as a cattle feed, traditional *S. cerevisiae* yeast was used in SSF, which was inhibited by limonene. The pretreatment has three purposes: 1) to remove limonene; 2) to sterilize the CPW; 3) to open up the structures of cell walls or polysaccharides.

Wilkins (2007a–c) studied the effect of D-limonene on the fermentation of CPW, and found that good ethanol yields could be achieved in 24 h if the limonene content was less than 0.12 wt%. Raw CPW usually contains approximately 0.8 to 1.6 wt% limonene, which means about 90% or more of the limonene needs to be removed to ensure that SSF will proceed successfully.

The second goal of pretreatment is to kill bacteria, which compete with yeasts for sugar and lower ethanol yields. Pretreatment also softens and breaks down cell walls, making the polysaccharides (pectin, cellulose, and hemi-cellulose) more accessible to enzymatic hydrolysis. It was noticed that raw peels separated from water quickly. As it can be seen in Figure 2, the particles of pretreated CPW were much smaller and softer compared to the raw CPW. This indicates that the size of pretreated CPW was fine enough for pumping and mixing during SSF, and therefore no grinding equipment was required in this process.

A major operating cost of pretreatment is steam consumption. Pilot plant studies were carried out to determine the optimal conditions for a pretreatment. For two pilot plant studies with different steam flow rates and feed rates, the removal of limonene, limonene content and dry weight in cooked CPW, and steam/limonene mass ratios are listed in Table 1. It was noted that a steam/limonene mass ratio of 8–10/1 was needed for limonene recovery from water emulsions (Braddock, 1999). In another study, Gerow (1974) reported that the optimal temperature for recovering limonene was in the range of 110 to 132 °C. Braddock concluded that limonene would decompose if the temperature was over 120 °C. Gerow also reported that a steam/limonene mass ratio of 3:1 was achieved using a complicated waste heat recovering system.

Table 1 shows that for pretreatment, the actual steam consumption was 30% to 50% higher than the theoretical steam consumption. The mass ratio of steam/limonene was 10 times higher than Gerow's results. It should be pointed out that instead of using
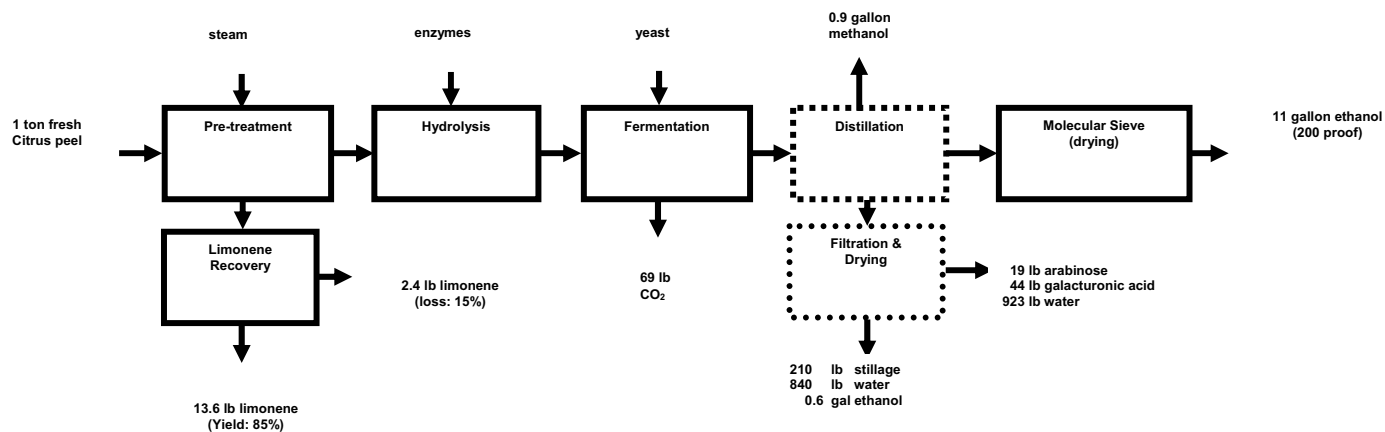

Fig. 1. Process block diagram for making ethanol from citrus processing waste (CPW).

Raw CPW　　　　**Pretreated CPW**

Fig. 2. Comparison of raw citrus processing waste (CPW) with pretreated CPW.

Table 1. Conditions and steam consumption of pretreatment [z, y]

Run	Feed rate (lb/min)	Limonene removed (lb/h)	Limonene (wt %)	Dry wt (wt %)	Actual steam (kg/h)	Limonene : steam ratio
1	8	4.5	0.071	19.60	91	1:46
2	10	5.6	0.074	20.13	84	1:33

[z]Limonene content in raw peel: 0.8 to 1.0 wt%.
[y]Organic solid in raw peel: 20.0 wt%.

CPW, Gerow used a mixture of limonene and water in his study. In our case, limonene was trapped inside the solid particles of CPW. Therefore, the actual steam consumption would be much higher than that required for stripping limonene from a water emulsion. In addition, extra steam was needed for moving CPW through the equipment, and to compensate for heat loss to the environment.

Table 1 also shows that under the studied conditions, pretreatment removed more than 90% of the limonene. Odio (1996) studied limonene recovery in the citrus industry, and found that in the production of citrus pulp pellets (CPP), approximately 50% of the limonene was emitted into the air as volatile organic compound (VOCs). If this new technology could be integrated with current citrus processes, lower amount of VOCs would be emitted into the atmosphere by the citrus industry.

The second part of the process is to hydrolyze cellulose, and to simultaneously ferment the resulting sugar into ethanol. Since the hydrolyzed sugars do not accumulate during SSF, cellulase can consume all of the cellulose without feedback inhibition by sugar, thus, resulting in a higher ethanol yield. Table 2 shows the ethanol yields at the beginning and end of a SSF. The maximum ethanol yield (4.05% w/v) was achieved in 18 h. According to the total sugar content in the peel, the maximum yield was equivalent to 90% of the theoretical ethanol yield. Mixing is critical at the beginning of SSF when the solid content and viscosity are high. Enzymes need to be thoroughly mixed with peel particles and make contact with all the cellulose and pectin in order to break them down.

After SSF, the resulting mash contained approximately 4% ethanol by weight and 10% residual solids. The heat transfer coefficient and heat capacity of fermented CPW were measured using a custom made heat exchanger, and the results are shown in Table 3. Due to the presence of pectin fragments, the fermented peel can be extremely viscous, and it is difficult to pass such viscous CPW through a traditional distillation column. Moreover, the efficiency of a distillation column is inversely proportional to the viscosity of peel. Distillation is an energy-intensive operation, and its efficiency is determined based on practical energy inputs as compared to theoretical steam requirements (Jacques, 2003). Therefore, it is worthwhile to optimize the SSF conditions, such that the resulting fermented peel is less viscous. This effort would be rewarded by increased efficiency of the distillation stage.

Table 3 shows the physical properties of fermented CPW. The apparent viscosity ranged from 14 to 38 N s/m^2 at 70 °C, depending on the shearing rates applied to the peel. The specific heat of fermented peel was 2.66 kJ/kg·K, much lower than that of the raw peel (3.77 kJ/kg·K, Charm, 1971). The estimated thermal conductivity of fermented CPW was 0.39 W/m^2 K, close to that

Table 2. Ethanol yield during simultaneous saccharification and fermentation (SSF).

Time (h)	Ethanol yield (% w/v)
1	0.14
3	0.33
5	0.77
18	4.05
20	4.05

Table 3. Physical properties of fermented citrus processing waste (CPW).

Viscosity	Specific heat	Thermal conductivity	Heat transfer coefficient
14–38	2.66	0.39	305–371
(N s/m^2)	(kJ/kg K)	(W/m^2 K)	(W/m^2 K)

of raw oranges (0.431 W/m K, Charm, 1971). The heat transfer coefficient of fermented peel was measured at 305–371 W/m^2 K and fell midway of the 60–600 W/m^2 K reported for viscous liquids (Bailey and Ollis, 1977). These data indicate certain constraints in the design and sizing of equipment when the process is scaled up. For viscous flow (>7000 cp) with a flow rate of 2 gal/min, the optimum inside pipe diameter was calculated to be 2 inches (Max, 1958).

Distillation and disposal of the residues is the last part of the process, and the economics are yet to be determined. The high viscosity, solid contents, and calcium salt in the fermented CPW complicate the distillation process. High viscosity reduces column efficiency. Organic solids could cause the buildup of charred insulation layers, and calcium salt could lead to scaling problem. Both charring and scaling could accumulate in the column, and thus decrease the vapor and liquid passages and cause a large pressure drop in the column. Consequently, the capacity and efficiency would be reduced, and eventually the tower would have to be shut down for cleaning. To overcome this a special distillation tower was designed strip ethanol from fermented CPW. The tower consisted of two columns: a stripping column and a rectification column. The striping column was a module of disc and donut (tray) alternatively stacked with equal space between each tray (Katzen et al., 1968). This design allowed vapor and liquid to have a widely open passage. Therefore, even when scale and other materials accumulated and fouled the trays, large volumes of vapor and liquid could still flow smoothly through the column without sacrificing the capacity and efficiency. The rectification column was a traditional packed column, which further concentrated the vapor from the stripping column. This system was designed to recover 95% of the ethanol in the fermented mash, and to yield an effluent stream containing 37% ethanol. The distillate was then transfered into a traditional distillation column, followed by a molecule sieve to yield a fuel grade ethanol.

This new process has been found technically viable for ethanol production from CPW. Continuous pretreatment and batch SSF have been demonstrated successfully on a pilot plant scale (10,000-gal mash/batch fermentation). Pretreatment removed more than 90% of the limonene in CPW at temperatures of 150 to 160 °C. Using SSF, a fermented mash containing 4% to 5% ethanol by volume can be achieved in less than 20 h. It has also been demonstrated that ethanol can be stripped off fermented CPW by single-stage batch distillation, but a continuous distillation for the removal of ethanol could be a challenge and further research is needed. Although ethanol production and limonene recovery from CPW, with subsequent drying of the residues left after distillation for use as a cattlefeed, is feasible, the long-term economic viability of this process can be greatly improved by the development of additional high-value co-products from the distillation residues.

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