d-LIMONENE RECOVERY

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INTRODUCTION

Oils have become an increasingly important by-product of the citrus processing industry. At the high prices reached last year and with good rates of recovery, one could get a dollar’s worth of oil out of a box of Valencia oranges, as shown in Table 1. No other commercially produced by-product of citrus processing comes close to these figures.

The quantity of oil as well as the price for the cold pressed and essence oils, change with varieties of fruit. For simplicity unless otherwise stated, I will talk about Valencia oranges.

In this same Table 1 we are assuming a total recovery of 10.35 lb. of oil/ton of fruit. If the fruit contains a total of 15 pounds of oil/ton this represents a 69% rate of recovery which with today’s high prices many processors are exceeding.

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Table 1. Valencia Oranges
Possible Oil Recovery Rates and Peak Commercial Value in 1995

<table>
<thead>
<tr>
<th></th>
<th>RECOVERY LBS/TON OF FRUIT</th>
<th>RECOVERY LBS/BOX OF FRUIT</th>
<th>APPROX. 1995 HIGH PRICE</th>
<th>VALUE/BOX IN US$</th>
</tr>
</thead>
<tbody>
<tr>
<td>COLD PRESSURED OIL</td>
<td>6</td>
<td>0.27</td>
<td>2.50</td>
<td>0.68</td>
</tr>
<tr>
<td>d-LIMONENE</td>
<td>4</td>
<td>0.18</td>
<td>1.75</td>
<td>0.32</td>
</tr>
<tr>
<td>ESSENCE OIL</td>
<td>0.35</td>
<td>0.016</td>
<td>4.00</td>
<td>0.06</td>
</tr>
<tr>
<td>TOTALS</td>
<td>10.35</td>
<td>0.466</td>
<td>1.06</td>
<td></td>
</tr>
</tbody>
</table>

For grapefruit, the value of the oils may exceed US $2.00/box which is quite significant.

Figure 1 illustrates the approximate seasonal average prices from 1989 until 1995, for d-limone and Valencia cold pressed oil. The sudden price increase for both products during 1995 was a welcome sight for the industry.

We need to point, as an added incentive to its recovery, that citrus oil can be very damaging to the operation of the processing plant's waste water treatment plant, because its very high COD value, in the order of 3,000,000 ppm, substantially increases oxygen demand, and also because it is a fairly good bactericide which can, even in small amounts, upset the bacterial balance of the treatment plant. I am sure that all of you are familiar with the problem.
Most every plant in the state, if not all, recovers oil in one form or another. Many have avoided recovering cold pressed oil totally or partially, because of the significant impact this has on waste water treatment investments.

Unfortunately, the problem now appears to be going beyond water pollution into air pollution. In November, 1990 amendments to the 1970 Federal Clean Air Act were signed into law. These amendments required stricter management of air sources in non-attainment areas; control of emissions from stationary and mobile sources; regulation of hazardous air pollutants; accidental release prevention and risk management; reduction in pollutants causing acid rain; a nationwide air permit program; protection of stratospheric ozone; stricter enforcement provisions, including civil and criminal proceedings punishable by fines and imprisonment, as well as many other provisions.

Like so many of the Federal environmental regulations the amendments to the Clean Air Act will have profound effects on the citrus processing industry. In late 1995 and early 1996, the citrus processing industry was just beginning to learn that many, if not all, processing plants would fall under the requirements of the Clean Air Act. Title V of the Clean Air Act requires that all facilities which discharge regulated air pollutants above certain quantities per year would be required to file for and operate under a new and much more comprehensive air permit program. The Florida DEP has presented preliminary information that indicates that many citrus processing facilities could be discharging in excess of 100 tons per year of VOC (volatile organic compounds). If a facility discharges in excess of 100 tons per year of VOC the facility is required to file for a Title V permit by June 15, 1996. Information was also presented that a few facilities may have been discharging in excess of 250 tons per year and because of this may face enforcement action or after-the-fact permitting requirements for their past actions. In addition to VOC discharges citrus processors may be discharging in excess of 10 tons per year of HAP (hazardous air pollutant) which is also a threshold level requiring a facility to apply for a Title V permit.

There is no question that all citrus processors should do whatever possible to try to be exempt from the provisions of Title V. If a processor can become exempt from the Title V permit requirement, the savings in future cost and headaches will be enormous. The easiest way to achieve this is in-plant recovery of the peel oils.

I want to talk about “steam distillation” of citrus oils as a non-contaminating substitute for cold pressed oil, or as a water pollution control measure for cold pressed oil recovery or as a means of reducing the processing plant’s VOC, or simply as another by-product of citrus processing that can significantly increase plant revenues.

To start, let’s look at what these oils are made out of and how they behave thermodynamically. This is essential to understanding how to recover them.

**d-LIMONENE**

This is the name of the organic compound which makes up about 95% of all orange and grapefruit oils. Its organic formula is illustrated in Figure 2.

The molecular weight of d-limonene (C10H16) is 136 and the boiling point at
atmospheric pressure is about 176°C (348°F). Therefore, d-limonene is not a low boiler, a common misconception. However, it follows "Dalton's Law" when boiled in the presence of water. This is called "steam distillation".

Figure 2. Organic Formula for d-Limonene

Dalton's Law states that in a mixture of ideal gases each component gas fills the entire volume of the mixture at the temperature of the mixture and at the partial pressure of that component (Unit Operations of Chemical Engineering by McCake and Smith).

To design a d-limonene recovery system, we have to calculate the ratio of d-limonene to water in the vapor. To do this, we need to know what the partial pressure of each compound is.

The following is a practical empirical formula that allows us to calculate the approximate partial pressure of d-limonene as a function of its temperature.

\[
\log_{10} P = 6.847 - \frac{1519.647}{(204.982 + T)}
\]

where \( P = \) absolute pressure in mmHg \& \( T = \) temperature in °C

Example: for \( T = 70^\circ C \) \( \rightarrow \) \( P = 20.92\text{mmHg} \)

for \( T = 100^\circ C \) \( \rightarrow \) \( P = 73.157\text{mmHg} \)

for \( P = 760\text{mmHg} \) \( \rightarrow \) \( T = 178^\circ C \)
We see from the above formula that at 70°C (158°F) pure d-limonene boils at an absolute pressure of 20.92mmHg (29.09 inches of Hg vacuum).

From the “Steam Tables” we can see that pure water at the same 70°C will boil at an absolute pressure of 233.74mmHg.

Therefore the mixture will boil as follows:

Pure d-limonene 70°C → 20.92mmHg
Pure water 70°C → 233.74
Mixture 70°C → 254.66mmHg which is the sum of the two partial pressures.

So, let’s work backwards now. If we go back to our formula we see that pure d-limonene at 254.66 mmHg boils at 137.20°C and from the Steam Tables we see that pure water boils at 72°C.

Therefore, if we have a d-limonene/water mixture in a 254.66mmHg atmosphere and we apply heat to this mixture, the temperature will rise until we reach 70°C at which point the mixture will start to boil until one of the two compounds is gone. The temperature will then increase again until it reaches the boiling point of the remaining compound. If water 72°C, if d-limonene 137.20°C.

In the citrus plants we always have far more water than d-limonene, therefore, we always run out of d-limonene first so that it effectively behaves as a low boiler.

To find out how much of each compound boils, we can rephrase Dalton’s Law to say that “the mole fraction of each compound in the vapor is directly proportional to its partial pressure.”

If we revisit our example that showed the absolute pressures corresponding to a 70°C boiling point for water, d-limonene and a mixture of both, and we chart them as illustrated in Table 2 we can see that d-limonene contributes 80% to the total pressure and water 92%. If we multiply these partial pressure percentages by the molecular weight of each compound, we arrive at the mass of each of the two compounds in the

<table>
<thead>
<tr>
<th>CONTRIBUTION TO TOTAL PRESSURE</th>
<th>MOLECULAR WEIGHT</th>
<th>MASS OF COMPOUND IN VAPOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PURE d-LIMONENE @ 70°C 20.92mmHg</td>
<td>136</td>
<td>10.88 40%</td>
</tr>
<tr>
<td>PURE WATER @ 70°C 233.74mmHg</td>
<td>18</td>
<td>16.56 60%</td>
</tr>
<tr>
<td>MIXTURE @ 70°C 254.66mmHg</td>
<td>27.44 100%</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Determination of The Composition of The Vapors That Boil From a d-Limonene/Water Mixture
mixture and from there we can easily calculate the percentage, which as illustrated in Table 2 results in 40% d-limonene and 60% water. Therefore, if we have a pure water and d-limonene mixture, regardless of the ratio of each compound, if we heat this mixture until it boils, the vapors that are generated will be 40% d-limonene and 60% water, by weight until we run out of one of the two compounds.

In real life, the mixture is not pure. The d-limonene is often trapped inside solid particles, therefore, we need to boil much more than theoretically indicated above to be assured of an efficient rate of recovery.

**RECOVERY**

The product that we refer to as d-limonene in the citrus plants is the steam distilled oil. We can recover this product in three different places in the plant:

**JUICE EVAPORATOR**

Figure 3 illustrates a typical T.A.S.T.E.® evaporator tube bundle.

The vapors from the previous effect enter the effect illustrated, at the bottom. As they move upward in the tube bundle, these vapors condense, releasing their heat and causing water to evaporate inside the tubes.

At the top of the bundle a small line allows the removal of the non-condensables, otherwise the bundle would eventually fill with air and/or CO₂ or other non-condensable and would stop working.

From the previous explanation we know that if d-limonene is present in the water we are removing from the juice it will boil first accompanied by the corresponding amount of water. The same logic tells us that as we condense the vapors, pure water will condense first until we reach that critical 60/40 ratio at which point d-limonene starts condensing.
condensing. If we size the non-condensables removal line large enough, then, in addition to removing the non-condensables, we can also remove the d-limonene plus the corresponding amount of water. This means that the d-limonene will not condense on the shell side of the effect, but will instead travel to the air removal system where we must trap it.

Figure 4 illustrates the air removal system. Here, the d-limonene vapors are compressed by the first air removal jet and delivered to a condenser where the d-limonene and accompanying water gradually condense until only the non-condensables are allowed to escape.

In some instances, we also place a second condenser after the second air removal jet to condense any remaining d-limonene at atmospheric pressure.

The product recovered this way is a small amount, but of excellent quality.

When the evaporator is equipped with essence recovery, instead of d-limonene we recover essence oil. A very valuable variation of the same oil.

**WASTE HEAT EVAPORATOR**

The Waste Heat Evaporator is where most of the commercially produced d-limonene in citrus plants comes from.

The main purpose of this evaporator is to concentrate the press liquor but these units are often sized large enough to handle other liquid effluents from the plant. Because the most highly contaminating of these is the cold pressed oil mill effluent due to its oil content, this too often finds its way to the Waste Heat Evaporator.

Citrus peel is treated with lime (calcium hydroxide) to break down the pectin and release the water. The lime also reacts with the ester aldelyde fractions of the oil. The oil recovered from this operation is considerably different in odor from the oil recovered from the T.A.S.T.E.® evaporator (Redd and Hendrix).

As shown earlier, in Table 1, an estimated 4 pounds of oil per ton of fruit are recovered here.

Figure 5 is one version of a Waste Heat Evaporator’s effect.

Here, as in the T.A.S.T.E.®, the oil laden vapors from the preceding effect enter the bundle at the bottom and move upwards through the lower section of the bundle. A substantial amount of vapor, possibly as much as 20%, is allowed to pass to the upper body. Here the flow is downward to encourage the condensing of d-limonene and to avoid reboiling.

The mixture that condenses is then fed into a decanter. The water phase out of the decanter is returned to the tube bundle to reboil and recover any oil that may have escaped. The oil phase is sent to the normal decanter in the bottom of the evaporator for further separation.
Figure 5. One Version of Waste Heat Evaporator Tube Bundle

The efficiency of steam distillation is somewhat dependent on the temperature to which the oil emulsion is heated. High temperatures help break it. Often we see Waste Heat Evaporators running too cold. This is generally due to an excessive amount of air in the vapor mixture going to the Waste Heat. This air normally enters through worn or inadequate dryer seals or through the dryer stack. This should be avoided because when this happens, the d-limonene is not efficiently removed from the press liquor. The result is a high oil content in the molasses. Those of you who sell your molasses to the alcohol industry know that this is objectionable because the bactericidal characteristics of the oil have a detrimental effect on the fermentation process.

Air should also be avoided because it often causes the evaporator to surge. When it does, d-limonene may condense in the lower portion of the tube bundle resulting not only in recovery losses but possible contamination of the waste water treatment system as well.

The d-limonene that escapes through the non-condensable removal line goes to the air removal system where it is recovered as we do in the T.A.S.T.E®.

OIL RECOVERY UNIT

The last means of steam distilling oil in the citrus plant that I want to touch on is a stand alone multiple effect unit with which many of you may not be familiar.

This is a steam driven unit; therefore, the emulsion is heated to higher temperatures than in the Waste Heat Evaporator, thus breaking the emulsions more efficiently resulting in very high recovery rates, in excess of 95% of the oil present. Generally speaking liquors processed through these units have only traces of oil left. This makes these units very useful as a deoiler prior to debittering.

Figure No. 6 illustrates a five effect version of one of these oil recovery units.
Figure 6. Five Effect Oil Recovery Unit

Here the oil laden liquor is fed through a series of stage preheaters, one after the last effect plus one before each effect. This allows us to preheat the liquor using the least amount of energy. From here the liquor goes through the five effects, transferring from one to the other by gravity. In each effect the liquor flashes which further helps drive the oil from the inside of solid particles.

The vapors from each effect go to the corresponding preheater where they flow upwards thus allowing most, if not all of the oil to continue on to the next effect where we have downward flow to encourage condensing of the oil and to avoid reboiling as we did in the top section of the Waste Heat Evaporator tube bundle.

All tube bundles have non-condensable removal lines. Here again, the oil that escapes through here is trapped in the air removal system.

This is a very energy efficient way of recovering oil. If we assume that we want to evaporate ten times more water than the oil that is present to assure virtual total recovery, then for every pound of oil recovered we evaporate 11 pounds. The five effect configuration should give us about 4.5 to 1 evaporation to steam ratio. This and a small amount of electricity are the only utilities required because the unit does not have air removal system or barometric condenser. It borrows this from a neighboring evaporator.

The total utility requirements are therefore about 2.5 pounds of steam per one pound of oil recovered. In more familiar units this means that we need 5,000 pounds of steam or about US $50.00 to recover one ton of oil with a value of some US $3,000.00.

This makes this unit quite attractive as a pollution control device particularly now that the EPA appears to be declaring war on d-limonene.
Through the use of units like the one described and by pressing the peel to low
moistures (in the low 60% range) some Brazilian processors claim total oil recovery
rates in excess of 90%.

Pressing the peel to low moisture is important because this reduces the mass going
to the dryer and with it the oil. Since approximately 50% of the d-limonene entering
the dryer is discharged into the atmosphere and is now counted as VOCs, reducing it at
the presses is most important.

Now is the time for the industry to increase its total oil recovery if not for its revenue
potential, at least to avoid falling in the 100 ton per year of VOC and having to file
for and operate under Title V permit or worse yet to avoid falling in the 250 ton per
year category which could carry far more serious consequences.

I hope to have give you some ideas of how to efficiently and economically
recover d-limonene.

There are other systems around the industry that are being used to recover
d-limonene. Generally, they require a lot of energy. Therefore, their utilization is
not wide spread and I did not feel that they warranted discussion.

NOTE: This paper was prepared using information supplied by Dr. Richard Jones
of Jones Edmunds and Associates and Mr. Phil Tope of Gumaco, Inc.