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Article

The Production of Vinyl Acetate Monomer as a Co-Product from the Non-Catalytic Cracking of Soybean Oil

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Abstract: Valuable chemical by-products can increase the economic viability of renewable transportation fuel facilities while increasing the sustainability of the chemical and associated industries. A study was performed to demonstrate that commercial quality chemical products could be produced using the non-catalytic cracking of crop oils. Using this decomposition technique generates a significant concentration of C₂–C₁₀ fatty acids which can be isolated and purified as saleable co-products along with transportation fuels. A process scheme was developed and replicated in the laboratory to demonstrate this capability. Using this scheme, an acetic acid by-product was isolated and purified then reacted with ethylene derived from renewable ethanol to generate a sample of vinyl acetate monomer. This sample was assessed by a major chemical company and found to be of acceptable quality for commercial production of polyvinyl acetate and other products.

Keywords: vinyl acetate monomer; fatty acids; crop oil; renewable chemicals; noncatalytic cracking

1. Introduction

Previous work has demonstrated that renewable transportation fuels can be derived from fatty acid and triacyl glyceride (TAG) based oils, such as crop oils, bacteriological lipids, and algae oils [1]. Along

with the well-established processes for biodiesel production [2], alternative processes are currently entering the marketplace that convert these oils into other fuels, such as jet fuel [3] and green diesel [1,4]. The margins for these processes are challenging as the competing petroleum refining industry is extremely efficient. One strategy to increase the economic fidelity of such processes is to produce a diversity of co-products, preferably with high values, leading to higher overall profit margins for the facilities.

Non-catalytic cracking leads to a number of such co-product options, including high purity carbon, aromatics, and short chain fatty acids [5]. Kubatova, *et al.* [6] found that the non-catalytic cracking of canola and soybean oils results in 15 wt%–25 wt% C₂–C₁₀ linear saturated monocarboxylic acids. These acids have market values that range from comparable to transportation fuels (C₂: acetic acid) to many times the value of fuels (C₇–C₁₀). Previous work [7,8] demonstrated that these acids can be separated from the alkanes, aromatics, and other constituents in the cracking reaction outlet liquid product. However, the question remained, “can products be generated that have sufficient purity for use in downstream product applications?” Thus the goal of the work documented here was to demonstrate one such product.

This goal was accomplished through the sponsorship and guidance of a major international chemical company, Kuraray America. In this work, commercial quality vinyl acetate monomer (VAM), which is the monomer used to produce polyvinyl acetate and other high-volume commodity materials [9,10], was produced from one of the most common of the short chain fatty acids, acetic acid. Figure 1 shows a simplified process scheme for those portions of a commercial facility that would be utilized to produce VAM. Soybean oil, a triacyl glyceride-based oil, is non-catalytically cracked and an organic liquid product (OLP) is recovered from the reaction products. Acetic acid is then extracted out of the mixture using an amine solvent and purified. The purified acetic acid is then reacted with ethylene and oxygen to form the VAM product.

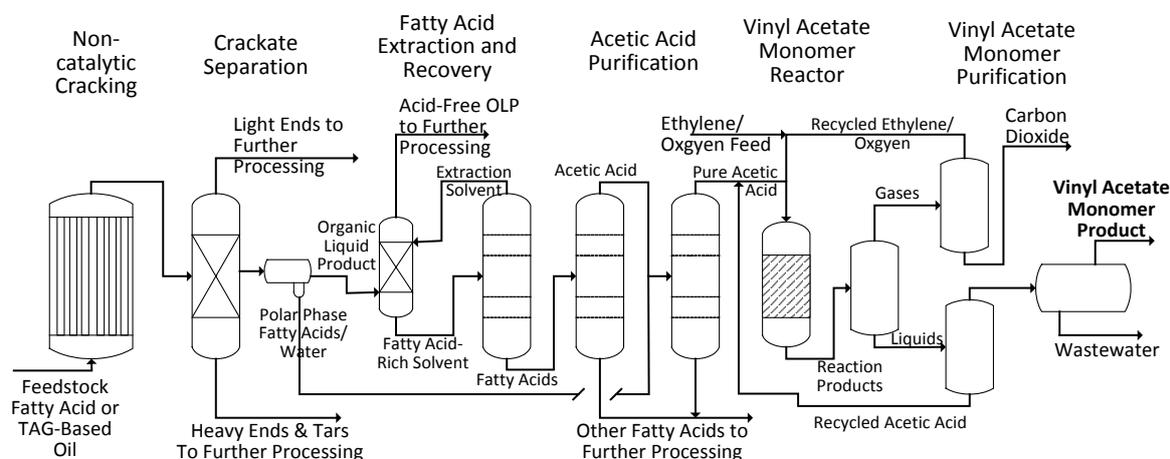


Figure 1. A simplified process scheme for the production of vinyl acetate monomer from a fatty acid or triacyl glyceride-based oil via non-catalytic cracking.

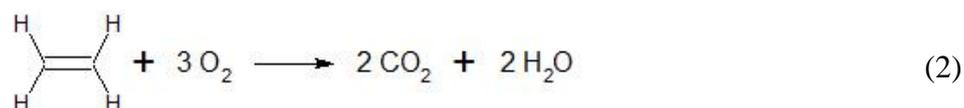
The largest user of acetic acid is the vinyl acetate monomer (VAM) manufacturing industry. VAM is the basis of white glue, laminating wallboard, and latex paint. Polymers derived from VAM are used in safety glass, film products, and hot-melt adhesives [11]. Although recent work has focused on alternative

methods [12], most VAM is produced by the oxidative addition of acetic acid to ethylene over palladium (Pd) based catalysts [13] as shown in Reaction (1):



This is an exothermic reaction with a standard heat of -176.2 kJ/mol [14]. Therefore, it is necessary to remove thermal energy during the reaction to maintain isothermal conditions.

Due to the presence of oxygen in the reactor, oxidation of ethylene can occur as an undesirable side reaction. This oxidation reaction is shown in Reaction (2):



This reaction has a high heat of reaction, -1322.8 kJ/mol, so it can complicate thermal energy removal [15]. The reaction also consumes the oxygen and ethylene that are meant for VAM production. For these reasons, this side reaction must be kept to a minimum.

Fortunately, the VAM Reaction (1) has a much lower activation energy, 30.5 kJ/mol, than the oxidation Reaction (2), 84.1 kJ/mol [15]. Thus, keeping the reactor temperature sufficiently low will reduce the rate of Reaction (2) relative to the rate of the Reaction (1). Also, since oxygen is a 3rd order reactant in Reaction (2) and only a half-order reactant in Reaction (1), keeping the O_2 concentration low helps to reduce the rate of ethylene oxidation. An O_2 concentration of less than 8% will also prevent an explosive mixture of ethylene and oxygen [16]. The need for such a low concentration of oxygen generally leads to low single pass conversions in the desired reaction.

Industrially, both gas and liquid phase reactions are used, but the gas phase alternative is much more common. The reaction is performed industrially using either a packed bed reactor (PBR) or a fluidized bed reactor [14]. The reaction is typically embedded within a large recycle loop [16]. Typically the reactor feed contains about 2–3 times the stoichiometric requirements for ethylene, but only about a quarter of the oxygen needed to convert the acetic acid to VAM. Therefore, oxygen is the limiting reactant. Single pass conversions for acetic acid and ethylene do not typically exceed 20% and 10%, respectively [14]. After the reactor effluent is cooled the product gases and liquids are separated using a knockout drum. Each stream is then processed further to recover unreacted feedstocks.

In the present work, a simplified scheme was followed which is more amenable to lab-scale implementation. Differences in this scheme from that outlined above are described in section 3, Experimental Methods, below.

2. Materials and Experimental Systems

2.1. Materials

Food grade soybean oil for thermal cracking was purchased from Columbus Oil (Chicago, IL, USA). Isobutyl acetate for the azeotropic distillation step was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA) and was 98% pure. Non-renewable acetic acid, which was used during commissioning and optimization of the VAM reaction steps, was at least 99.7% pure and was purchased from VWR

International (Radnor, PA, USA). Palladium-gold catalyst was provided by Evonik Industries (Parsippany, NJ, USA).

Although ethylene is also a by-product of TAG oil non-catalytic cracking, the present work focused on renewable acetic acid generation. Both renewable and non-renewable ethylene were used in the second reaction step to form the VAM. Renewable ethylene can be produced from ethanol by dehydration over a catalyst at high temperatures [17] or by a proprietary process involving a butylene intermediate developed by Braskem [18,19]. Oxygen and non-renewable ethylene were both 99.9% pure and were purchased from Praxair Inc. (Danbury, CT, USA). Renewable ethylene was produced by Braskem for Kuraray America (Houston, TX, USA) to a 99.9% purity from ethanol at Braskem's plant in Triunfo, Rio Grande do Sul, Brazil.

Analytical standards and solvents (methanol, butanol, acetic acid, propionic acid, butanoic acid, and pentanoic acid) were purchased from Sigma Aldrich (St. Louis, MO, USA) and were all 98.5% pure or greater. Vinyl acetate standard was purchased from VWR international (Radnor, PA, USA) and was 99% pure. Chromatography gases—helium, hydrogen, argon, and air—were all obtained from Praxair (Danbury, CT, USA) and were 99.999% pure unless otherwise specified.

2.2. Experimental Systems

A series of lab-scale systems were used to replicate the processing scheme shown in Figure 1. Both reaction steps were performed using continuously operated systems, while the extraction and purification steps employed both continuous and batch processing systems. Each major step was performed separately so the quality of the intermediates could be analyzed and optimized prior to performing the next step.

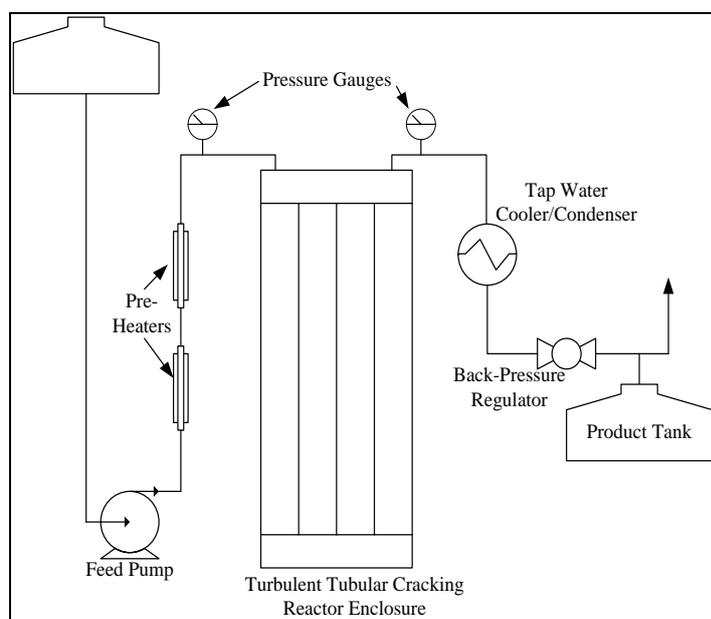
The most significant difference from the flow scheme shown in Figure 1, was the use of water as the fatty acid extraction solvent (following Ghandi *et al.* [7]) rather than an amine (as per Braegelmann *et al.* [8]). Amines allow nearly complete extraction of all of the fatty acids in the mixture [8] whereas hot water is only very efficient for acetic acid [7]. Since we were only interested in utilizing the acetic acid by-product in this project, use of water simplified the downstream purification steps compared to using an amine. Commercially, it would make more sense to extract all of the fatty acids and then purify those that are commercially attractive into high value chemical products with the remaining fatty acids deoxygenated to alkanes and used in fuel products.

In the present work, a two phase mixture was produced from soybean oil in a non-catalytic cracking reactor and then separated into four phases: A non-condensable gas phase, an aqueous liquid phase, an organic liquid product phase (the dominant phase), and a heavy organic liquids phase. Short chain fatty acids were extracted from the organic liquid product phase via extraction into water. A nearly pure acetic acid stream was produced by azeotropic distillation and combined with the aqueous liquid phase from the cracking reactor which was nearly pure acetic acid. A final distillation step was performed to reach the target acetic acid purity of 98 wt%. The renewable acetic acid was reacted with oxygen and ethylene over a Pd-Au catalyst to produce VAM. The VAM was recovered from the unreacted feed materials, which were then recycled to the reactor.

The specific lab-scale systems used for each of these steps is described below.

2.2.1. Feed Oil Cracking

Non-catalytic cracking was carried out in a small pilot-scale 2 L/h continuous tubular reactor held in an insulated ceramic enclosure containing electric heating elements with a total heat output of about 6000 W, as shown in Figure 2. Soybean oil was routed through two preheaters and then fed to the reactor using a Neptune model 515-A-N3 proportioning pump. The tubular reactor consisted of 16 sections of 1.5 m long 0.95 cm diameter Inconel 625 tubing. The tubes were connected by manifolds on both ends so that the oil would flow through 24.4 m of tubing while being cracked. The temperature was monitored using eight thermocouples in the enclosure and three thermocouples in the fluid. Fluid temperature was controlled via LabVIEW (National Instruments, Austin, TX, USA) by regulating the current supplied to the heating elements. The reactor pressure was monitored using PX309-1KG5V pressure transducers (Omega Engineering Inc., Stamford, CT, USA). Reactor pressure was maintained manually using a back-pressure regulator (Swagelok, Solon, OH, USA) and products were condensed and cooled using a shell and tube heat exchanger with a high flow rate of cold water before collection in the product tank.



(a)



(b)

Figure 2. Diagram (a) and photo (b) of the University of North Dakota's pilot scale continuous tubular non-catalytic cracking reactor.

2.2.2. Cracking Product Liquid Distillation

The liquid collected in the product tank of the cracking reactor was distilled continuously in an insulated 1.83 m tall, 10.2 cm diameter distillation column packed with 1.27 cm ceramic rings as shown in Figure 3. The column's feed was approximately 0.91 m from the bottom of the column. An electric heat source was wrapped around the bottom 15 cm of the column. The overhead temperature was monitored using a thermocouple in the vapor phase distillate stream and controlled by varying the heat supplied in the bottom of the column. Distillates were condensed in a water cooled heat exchanger and recovered in a distillate receiver drum. The bottom of the column was operated in a semi-batch manner.

A valve was opened to allow the bottoms product to flow out when the level in the column reached 0.3 m, which was indicated by a side draw. The aqueous phase from the distillate stream was decanted off of the organic phase using a separatory funnel.

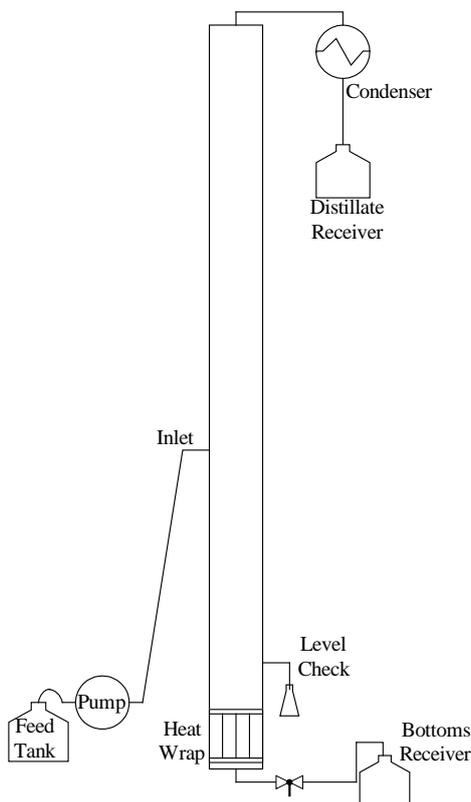


Figure 3. Schematic of the UND bench-scale continuous crackate distillation column.

2.2.3. Extraction of Organic Phase Acetic Acid

Extractions were performed in a 2L separatory funnel. The organic phase distillates from the crackate distillation were mixed with specific amounts of deionized water. The mixture was then allowed to phase separate and the aqueous phase was decanted off of the organic phase using a separatory funnel.

2.2.4. Azeotropic Distillation of Aqueous Acetic Acid

The first purification step was accomplished through the removal of water by azeotropic distillation using isobutyl acetate (IBA) as an entraining agent for water. This distillation was carried out in a lab-scale distillation apparatus with a 5 L round bottom pot flask and a 30.5 cm tall, 2.5 cm diameter glass column packed with 0.64 cm ceramic rings as shown in Figure 4. The distillate was condensed using a water-cooled glass condenser, and then entered a separatory funnel where water was removed while IBA was periodically refluxed into the distillation column using a peristaltic pump. Waste water from the separatory funnel was disposed.

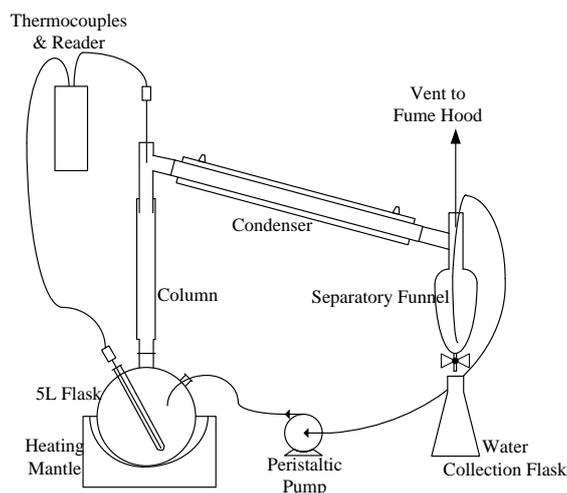


Figure 4. Diagram of the initial acetic acid recovery step using a lab-scale recycle distillation system.

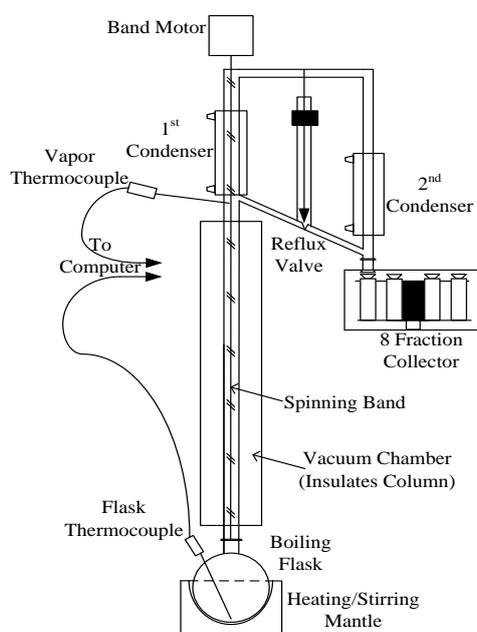


Figure 5. Diagram of the automated spinning band distillation system used for the second step in the acetic acid recovery process.

The second purification step was performed using a High Efficiency Distillation System (Model 18–100, B/R Instrument, Easton, MD, USA) as shown in Figure 5. The distillation column was equipped with a Teflon spinning band capable of producing up to 200 factory reported stages of separation. An 8 receiver fractionating carousel was used to automatically collect fractions based on overhead temperature.

The spinning band distillation system shown in Figure 5 was also used to separate VAM from acetic acid and wastewater (the final step shown in Figure 1).

2.2.5. VAM Production

The VAM reactor system is shown in Figure 6. The reaction vessel consisted of a 2.5 cm diameter, 35.5 cm long tubular packed bed reactor jacketed with a 5 cm diameter shell for water cooling. Acetic acid was fed using a high pressure positive displacement pump with a maximum flow rate of

10.0 mL/min. Gas phase reactants and inerts were fed through thermal mass flow controllers and all reactant streams were mixed together before entering the reactor. Both utility water and process streams were pre-heated in 0.64 cm steel tubing coils inside insulated ceramic enclosures containing electric heating elements. Both utility and process streams were also cooled after the reactor using water-cooled heat exchangers.

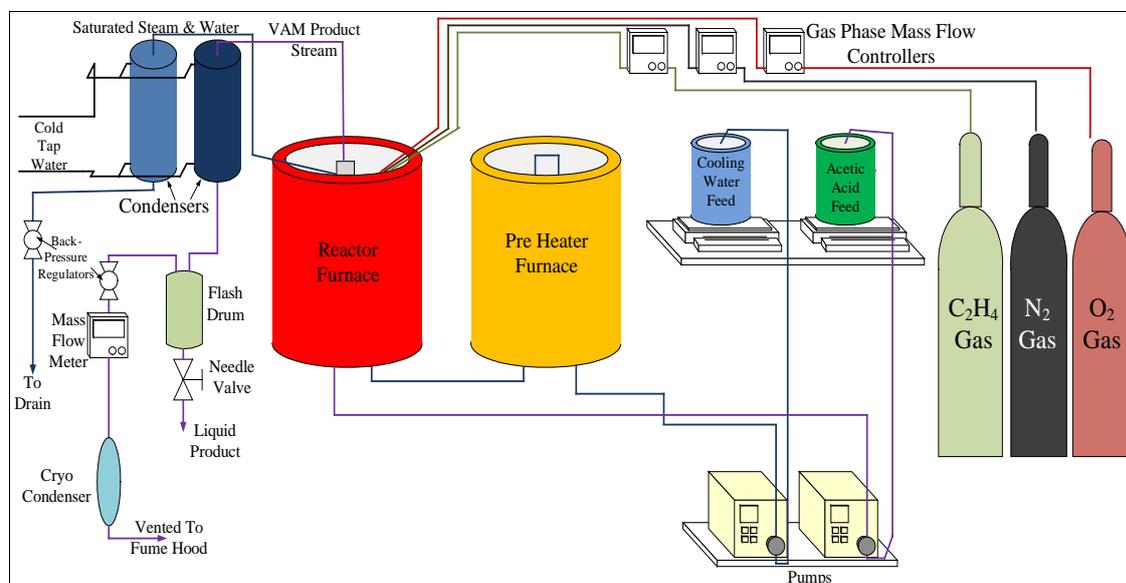


Figure 6. The VAM reaction system.

Temperatures in the process and utility streams were monitored before and after the reactor using k-type thermocouples. Reactor temperature was measured using a thermocouple inserted directly into the bed, and controlled by the back-pressure of the water/steam jacket. Utility water was heated to near saturation before entering the jacket, at which point the heat of reaction would vaporize some of it to steam.

3. Experimental Methods

3.1. The Production of High Purity Renewable Acetic Acid from Soybean Oil

Soybean oil was routed through the preheaters at an inlet flow rate of 1 L/h to increase its temperature to 385 °C before the oil entered the cracking reactor (Figure 2). The oil was cracked at 430 °C and 1720 kPa. The cracking reactor product was cooled against room temperature water (around 25 °C). Non-condensable gases and highly viscous tars were separated from the liquid in a settling drum.

The liquid product was continuously distilled at an average rate of 40 g/min using the system shown in Figure 3. The light key in this distillation was acetic acid which was recovered at an overhead vapor temperature of approximately 140 °C. Distillates were condensed in a water cooled heat exchanger and recovered in a distillate receiver drum. The aqueous phase from the distillate stream was decanted off of the organic phase using a separatory funnel.

Organic phase distillates from the crackate distillation were washed four times with distilled deionized water. The first wash was performed using a 50:1 ratio of distillates to water. The following washes used 75:1, 100:1, and 100:1 distillate to water ratios. The relative amount of water was reduced

in each wash to maintain concentrated extract while removing acetic acid from a more and more dilute source. While lower in concentration than acetic acid, propionic and, to a lesser extent, butyric acid were also partially extracted during this process.

The acetic acid-rich water mixture was then purified using a two-step distillation process. In the first step, acetic acid was concentrated in a batch distillation system (Figure 4) using IBA as an entraining agent for the water. The aqueous acetic acid solution was concentrated in 2 L batches with 200 mL of IBA added to each batch. Each batch was distilled until 1 L of water had been removed. At this point, the IBA recycle was stopped and the remaining IBA was distilled out of the more concentrated acetic acid solution.

To achieve the high purity specification for VAM-grade acetic acid, a high reflux batch distillation (Figure 5) was used to purify the acetic acid and to separate it from the heavier (C3–C5) carboxylic acids. During fractionation water was distilled off primarily in the first fraction. As the water remaining in the acetic acid solution was removed overhead, the acetic acid and heavier compounds were concentrated in the pot. As the distillate temperature increased, fractions of gradually increasing acetic acid concentration (and less water) were recovered until 118 °C, the boiling point of acetic acid. After this point, the fraction of acetic acid in the distillate product fractions decreased as the percentage of propionic acid increased. The fraction collected for the range from 115 °C to 121 °C contained a high concentration of acetic acid, in excess of 85 wt%. However, the semi-purified fractions containing 2 wt%–85 wt% acetic acid (and either water or propionic acid as the balance) accounted for a larger volume of product. The semi-purified fractions were then further purified in subsequent distillations, which resulted in additional semi-purified fractions. Full purification of the renewable acetic acid required an iterative procedure using many batch distillations.

3.2. The Production of Renewable VAM from Acetic Acid, Ethylene, and Oxygen

VAM was produced by the oxidative addition of AcOH to ethylene in a continuous packed bed reactor (Figure 6) containing Pd-Au catalyst supported on silica and promoted by potassium acetate [13]. The system was commissioned and optimized using commercially available non-renewable resources prior to using the system on renewable acetic acid and ethylene.

The goal with each pass through the reactor was to convert all of the oxygen via Reaction (1) and achieve maximum conversion of acetic acid in order to reduce the number of reaction cycles. Thus, it was favorable to increase the amount of oxygen fed relative to the amount of acetic acid. However, it was still necessary to keep the gas phase reactants below the limits of an explosive mixture, meaning that the oxygen concentration was limited to 8 mol% or lower on an acetic acid-free basis [16]. There are two ways to accomplish this: (1) the amount of ethylene and oxygen can be increased together, increasing the excess ethylene that will be vented or (2) an inert gas can be added to the gas reactants diluting the oxygen in the gas phase, but still increasing it relative to acetic acid in the liquid phase. Since the renewable ethylene supply was limited, N₂ was added to the reactant stream to dilute O₂ below to explosive limit.

The reaction was carried out at a pressure of 550 kPa and a temperature of 135 °C. Acetic acid was fed to the reactor at 0.7 mL/min. Gas phase reactants were fed at the following flowrates: 748 standard cubic centimeters/minute (sccm) ethylene, 77 sccm oxygen, and 353 sccm nitrogen. At these rates,

ethylene has a 2.5:1 molar ratio with acetic acid, and the gas phase oxygen concentration is 6.5 mol%. One hour runs using renewable acetic acid with both renewable and conventional ethylene were monitored, and the average effluent flow and composition were determined.

Using these conditions acetic acid conversion was kept above 30% which is slightly higher than in commercial processes. This gain was achieved by having a much longer residence time (about 40 s) than typical commercial processes (about 10 s). The VAM reactor effluent contained 30 wt% VAM on average. Renewable acetic acid was reacted with ethylene at the chosen conditions to produce one kg of vinyl acetate monomer (VAM).

VAM and water were distilled out of the unreacted acetic acid using the B/R 18–100 distillation column shown in Figure 5. The first fraction containing VAM and water was taken from 45 °C to 95 °C. Water was then separated from the VAM product using a separatory funnel. An additional fraction from 95 °C to 102.5 °C was taken to remove any additional water from the acetic acid so that it could be reused in the VAM reactor. This cycle of react and recover had to be repeated several times before the desired amount of the acetic acid was converted to VAM.

The VAM product from this distillation was recovered over a wide interval to ensure that all of the desired product was recovered. An additional distillation was used to further purify the VAM, removing small amounts of water, acetic acid, and other impurities. The final 1 kg sample VAM product was approximately 99 wt% pure. All acetic acid used to produce this final product was derived from the original soybean oil.

4. Analytical Methods

4.1. Liquid Phase GC Analysis

Analysis was performed on a Perkin Elmer Clarus 480 Gas Chromatograph equipped with a split/splitless injector and a flame ionization detector (FID). Helium was used as a carrier gas under constant inlet pressure control at 101.3 kPa. Using a 10 µL syringe, 0.6 µL volumes of each sample were manually injected at 300 °C using split mode with a split ratio of 30:1. Separations occurred on a Restek Stailwax-DA 30m long 0.25 mm ID column with a film thickness of 0.25 µm. The column temperature was held initially at 40 °C for 2 min, and then increased at a rate of 15.0 °C/min to 135 °C. Next the column oven was ramped to 225 °C at a rate of 40.0 °C/min where it was held for 3 minutes. The FID was operated using a hydrogen flow of 45 mL/min and an air flow of 450 mL/min.

Aqueous samples and standards were prepared by dilution in isopropyl alcohol, with the addition of butanol as an internal standard. Five point calibrations were used for each analyte: C2–C4 short chain fatty acids, isobutyl acetate, and vinyl acetate. The linear calibration curves each had a high degree of fit with R^2 values greater than 0.996. Analytes were quantified based on their peak areas relative to the peak area of the internal standard.

4.2. Gas Phase GC Analysis

Gas phase products of the thermal cracking and VAM reactions were analyzed using an SRI 9610C gas chromatograph. The splitless chromatograph injector was maintained at a temperature of 192 °C. 100 µL injections were made manually using a 1mL syringe. Separations were performed using an

2.4 m Hayasep D packed column with Ar carrier gas maintained at a constant pressure of 83 kPa. Analytes were detected using an FID with a methanizer maintained at a temperature of 375 °C. The column oven was held at a temperature of 40 °C for 2 min, then ramped at 20 °C/min to 250 °C, and held for 15 min.

The sample compositions were normalized to 100% neglecting the water vapor, O₂, and N₂ in each sample. Response factors for each compound were determined using a manually prepared calibration gas standard consisting of a mixture of H₂, CO, CO₂, and C₂H₄ diluted in Ar.

5. Results and Discussion

5.1. Acetic Acid Production and Extraction

The non-catalytic cracking of soybean oil was carried out at conditions based on earlier research [5]. The product of these reactions had a composition typical of previous TAG oil crackate [5] at the chosen conditions (not shown). The product crackate from the non-catalytically cracking of soybean oil yielded 89 wt% condensable liquids and 11 wt% non-condensable gases. Because the focus of the present work was on acetic acid recovery, the organic liquid product distilled from the crackate was lighter in molecular weight and lower in yield than those reported in previous work [5,6]. The organic liquid product (OLP) recovered was 24.5 wt % of the feed crackate. Aqueous distillates accounted for 1.5 wt% of the feed crackate. The aqueous distillates were analyzed for short chain fatty acids using liquid phase GC analysis which indicated an acetic acid concentration of 28 wt%. Based on the quantities extracted, the OLP and crackate acetic acid concentrations were back calculated to be 1.9 wt% and 0.89 wt%, respectively. About 250 L of soybean oil were cracked to produce about 1.6 L of acetic acid.

The OLP was washed several times with deionized water to extract its acetic acid in a separatory funnel. The aqueous extracts collected from each wash were analyzed separately for short chain fatty acids by liquid phase GC. The aqueous wash water contained water, C₂ to C₅ linear saturated carboxylic acids, and trace amounts of dissolved hydrocarbons. The concentrations of acetic acid contained in the aqueous extract from each water wash are shown in Table 1. The concentration in the extract solutions was successfully kept high by using small amounts of water in a series of several extractions. The success of multiple stages suggests a continuous counter-current extraction scheme would be an efficient design to recover acetic acid when water is used as the extracting solvent.

Table 1. Acetic acid concentration in aqueous extracts from the organic liquid product (OLP) generated by the non-catalytic cracking of soybean oil.

Aqueous Washes	Distillates to Water Ratio	Acetic Acid in Extract (wt%)
Wash 1	50:1	25.7
Wash 2	75:1	22.8
Wash 3	100:1	18.6
Wash 4	100:1	18.5

Azeotropic distillation with IBA was used to concentrate the acetic acid content of the aqueous extracts to approximately 40 wt%. The concentrated product was further processed via batch distillation

to purify the acetic acid. Purification was carried out via multiple 0.5 L batch distillations and resulted in several fractions containing varying concentrations of acetic acid. A breakdown of these fractions is shown in Table 2.

Table 2. Acetic and propionic acid concentrations in various 1st step distillation fractions produced from Table 1 aqueous extracts.

Fractions	Temperature Range	Mass (g)	Acetic Acid Concentration (wt%)	Propionic Acid Concentration (wt%)
Feed	-	500	40%	Not Analyzed
1	<100 °C	75	12%	0%
2	100–105 °C	250	22%	1%
3	105–115 °C	60	70%	4%
4	115–121 °C	70	89%	7%
5	121–130°C	45	72%	22%

Fractions 2, 3, and 5 (Table 2) were recombined with an additional 40 wt% pure acetic acid (from the subsequent distillation step) and redistilled in the same manner to increase the overall yield of ~90 wt% pure AcOH. The 90% concentrated AcOH was distilled using the apparatus shown in Figure 5 to obtain a 98 wt% pure fraction as well as additional lower-purity fractions. Those lower purity fractions were subsequently recombined with other fractions and redistilled. This process of combining and redistilling lower purity fractions, while keeping high purity fractions, was repeated several times to generate the desired volume of acetic acid. The final product consisted of 1.6 L of 98 wt% pure acetic acid with about 2 wt% propionic acid and only trace amounts of water.

Laboratory limitations made purification a time intensive process and resulted in a product that was only moderately pure (98 wt%). Continuous distillations using a low boiling azeotrope entrainer to reach higher purities efficiently are common in industry, so it is likely that a continuous distillation system could purify acetic acid to greater than 99 wt%. Continuous azeotropic distillation is commonly used to recovery acetic acid from aqueous solutions in the terephthalic acid industry [20]. This conclusion was verified by process simulation, demonstrating that these lab-scale inefficiencies and challenges can be overcome by well controlled continuous separation, as is possible in a larger scale system. Despite these limitations, this quality of acetic acid was found to be an acceptable feedstock for the VAM production reactor system employed.

5.2. VAM Production and Purification

The VAM reaction was optimized using conventional acetic acid and ethylene, along with high purity oxygen. Adding an inert gas (nitrogen) to the reaction mixture allowed the oxygen flow rate to increase relative to the acetic acid flow rate without increasing the gas phase oxygen concentration. As a result, for a given conversion of oxygen, conversion of acetic acid was higher than from commercial scale reactors, yet the concentration of oxygen remained below the explosive limit. However, adding an inert gas also reduced the concentrations of the other reactants, and thus, the driving force for the desired reaction. This was offset by using a much longer residence time than in a commercial scale system.

Reaction temperatures, pressures, and feed compositions in the lab-scale reactor gave good results at values similar to typical industrial conditions [16].

One hour runs were then conducted using the 98 wt% pure renewable acetic acid with both renewable and conventional ethylene. The results are shown in the Table 3. The VAM concentrations from both runs were nearly identical and well within the variation limits of the experiments. The effluent from the renewable ethylene contained slightly less acetic acid. It is possible the absorption of acetate onto the catalyst was greater in that trial, resulting in an accumulation of acetate onto the catalyst.

Table 3. A comparison of VAM concentrations in the VAM reactor liquid effluent with renewable acetic acid and either renewable or conventional ethylene

Ethylene Feed Type	Rate of Liquid Product Generation (g/min)	Acetic Acid Concentration (wt%)	VAM Concentration (wt%)
Renewable Ethylene	1.128	54.2	25.3
Conventional Ethylene	1.131	60.6	25.8

The VAM reactor system was used to generate sufficient effluent to produce a 1 kg sample of purified VAM. The liquid product stream from the packed bed reactor contained VAM, acetic acid, and water.

VAM and water form a low boiling azeotrope and could be recovered from VAM reactor liquid effluent using the batch distillation system shown in Figure 5. The first fraction containing VAM and water was taken from 45 °C to 95 °C. Water was then separated from the VAM product using a separatory funnel. An additional fraction from 95 °C to 102.5 °C was taken to remove any additional water from the acetic acid so that it could be reused in the VAM reactor. This cycle of react and recover was repeated several times before the desired quantity of acetic acid was converted into product. The VAM product from this distillation was recovered over a wide interval to ensure that all of the desired product was recovered. An additional distillation was used to further purify the VAM, removing small amounts of water, acetic acid, and other impurities. The final 1 kg sample VAM product was approximately 99 wt% pure.

6. Conclusions

This project has successfully demonstrated how a valuable chemical by-product can be produced from the non-catalytic cracking of a fatty acid or triacyl glyceride-based oil. Specifically, acetic acid was isolated from the cracking reactor product stream, purified, and converted into vinyl acetate monomer. The 1 kg VAM product sample was sent to Kuraray CO., LTD's central research laboratories in Japan for evaluation. Kuraray indicated that the sample passed all of their internal proprietary quality control tests [21].

All of the laboratory-scale steps utilized have commercial analogs, confirming that this is a commercially viable pathway for the production of renewable VAM. Comparison tests demonstrated that the use of renewable ethylene derived from ethanol gave nearly identical results as conventional ethylene.

The ability to produce valuable co-product chemicals increases the economic fidelity of a renewable or biofuels facility. This work demonstrates that these advantages are likely to accrue to processes based on non-catalytic cracking pathways.

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Author Contributions

Benjamin Jones co-wrote the paper, designed and built the experimental systems, conducted the experiments and performed the analytical work.

Brian Tande assisted in evaluation and interpretation of the results and edited the paper.

Michael Linnen designed and constructed the non-catalytic cracking unit and assisted in the design and construction of the other experimental systems utilized in this work.

Wayne Seames co-wrote the paper, conceived the project, provided the basic framework for the experiments, and coordinated the total work effort.

Conflicts of Interest

The authors declare no conflict of interest.

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