THESIS

AN ECONOMIC AND ENVIRONMENTAL ASSESSMENT OF GUAYULE RESIN CO-PRODUCTS FOR A US NATURAL RUBBER INDUSTRY

Submitted by

Brooke Silagy

Department of Chemical & Biological Engineering

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Master's Committee:

Advisor: Kenneth Reardon
Co-Advisor: Jason C. Quinn

Matthew Kipper
Thomas Bradley

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ABSTRACT

AN ECONOMIC AND ENVIRONMENTAL ASSESSMENT OF GUAYULE RESIN CO-PRODUCTS FOR A DOMESTIC NATURAL RUBBER INDUSTRY

Guayule (*Parthenium argentatum*) is a natural rubber producing desert shrub that has the potential to be grown in semi-arid areas with limited water resources. Numerous studies have examined the costs and environmental impacts associated with guayule rubber production. These studies identified the need for additional value from the rubber co-products, specifically the resin, for sustainable and commercial viability of the biorefinery concept. This study developed process models for resin-based essential oils, insect repellant, and adhesive co-products that are integrated with sustainability assessments to inform commercialization strategies. A techno-economic analysis and cradle-to-gate life cycle assessment (LCA) of these three different co-product pathways assumed a facility processing 66 tonnes/day of resin (derived from the processing of 1428 tonnes per day of guayule biomass) and included resin separation through co-product formation. The evaluation outcomes are integrated into an established guayule rubber production model to assess the economic potential and environmental impact of the proposed guayule resin conversion concepts. The minimum selling price for rubber varied by co-product: \$3.54 per kg for essential oil, \$3.40 per kg for insect repellent, and \$1.69 per kg for resin blend adhesive. The resin blend adhesive co-product pathway had the lowest greenhouse gas emissions at 5.54 kg CO_2 eq per kg rubber, evaluated with a combined displacement and economic allocation. These findings show that the resin blend adhesive pathway supports the development of a biorefining concept that can catalyze a U.S.-based natural rubber industry.

ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

Guayule is a desert, perennial shrub that produces natural rubber and can be cultivated in the southwestern U.S. Currently, over 90% of natural rubber comes from the hevea tree (*Hevea brasiliensis*) produced in southeastern Asia [45]. Concerns with disease, security and increasing global demand of natural rubber necessitate a domestic, alternative source of natural rubber. Additionally, guayule requires less water than other commercial crops and may help farmers in the region adapt to increasing water shortages [39]. Although efforts to commercialize guayule have been long ongoing, major barriers to commercialization have been economic factors, such as production costs, and lack of processing infrastructure [35]. An integrated biorefinery that takes advantage of guayule's co-products has the potential to overcome these economic barriers.

Guayule offers bagasse and resin as co-products that have the potential to improve the economic and environmental impact of a guayule biorefinery. Previous studies have explored the use of bagasse in various industries, however, the potential products from bagasse are of limited overall value. The implications of resin co-products for the sustainability of the system remain uncertain. Recent research has characterized the chemical composition of guayule resin, assessed separation methods, and identified potential applications [10]. Given the unique chemical composition of guayule resin, many co-product pathways have been proposed, yet no pathways for scale up have been empirically investigated.

Among the natural resin products, three were identified as having the greatest likelihood for commercialization based on their market size and product price: essential oils, bio-based insect repellants and resin blend adhesives. One of the key factors for resin commercial viability is the presence of volatile fractions, specifically monoterpenes (alpha-pinene, beta-pinene, d-limonene), that are used in many commercial products, including aromatherapy, cosmetics, and the food and beverage industry [40]. Guayule resin has been found by Dehghanizadeh et al. (in review) to have biopesticide activity against cockroaches. Guayule resin can also be blended with urea formaldehyde (UF) to produce a strong bio-based adhesive with good impact resistance and hardness [26]. The proposed resin blend adhesive can be used directly in various industries, including woodworking, furniture manufacturing, construction, automotive, and textiles [56].

This study aims to provide a more comprehensive analysis of these three products' potential for value-add to support the commercialization of a guayule-based biorefinery by integrating process models with techno-economic analyses (TEA) and life-cycle assessment (LCA). The first process involves multi-stage, multi-component vacuum distillation of guayule resin to isolate essential oils. The second entails single-stage, multi-component vacuum distillation of the resin to extract fractions with potential as insect repellent. The third investigates a blend of guayule resin and UF to form an adhesive. For all three resin co-products, low-molecular weight rubber (LMWR) is extracted from the resin mixture before processing (**Error! Reference source not found.**). The two novel contributions of this work are the first TEA of guayule resin-to-product pathways and the first integrated LCA and TEA comparison across multiple resin-to-product pathways including guayule production, harvest, and biorefining. From these contributions, conclusions about each pathway's economic potential and environmental implications can provide valuable information for research and development, specifically, the identification of the most promising co-products to minimize the costs and environmental impacts associated with guayule rubber production and to support an alternative natural rubber industry.

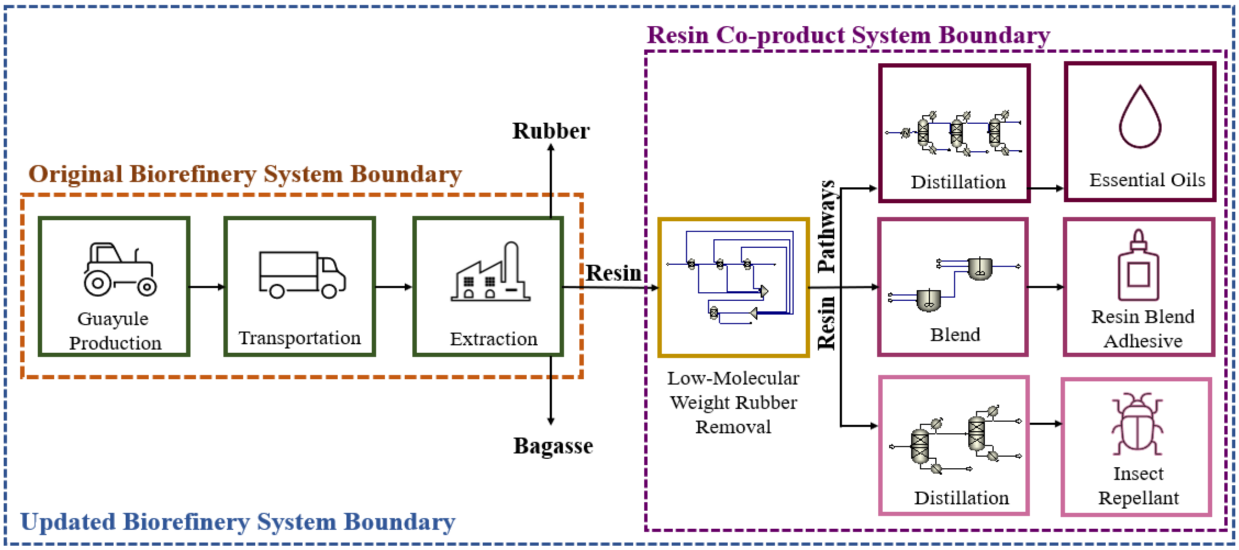

Figure 1: Process flow diagram of the techno-economic and life cycle assessment performed on a guayule-based biorefinery concept. The initial system boundary is expanded to include removal of low-molecular weight rubber and three different resin conversion co-product pathways: essential oils, resin blend adhesive, and insect repellant.

CHAPTER 2: METHODS

Simulations of commercial-level process models for three resin co-product pathways were developed using Aspen Plus® V11 [4] with existing literature and bench-scale experiments for model validation. Capital and operating costs were calculated and environmental impacts were evaluated based on life cycle methodology with global warming potential (GWP) determined for each pathway. Economic and environmental results for the three pathways were integrated with an existing biorefinery model (developed using Microsoft EXCEL [47]) using the discounted cash flow rate of return method to determine minimum rubber selling prices (MRSP) and greenhouse gas emissions on a per kg rubber basis.

Process Modeling

The design of the three resin co-products was conducted utilizing Aspen Plus V11 as the primary simulation method for defining the mass and energy balances used as inputs to sustainability modeling. The three resin co-product process models were developed based on bench experimental work conducted. Aspen Plus is a software tool useful for modeling, simulating, and optimizing chemical processes [4]. Aspen Plus offers several significant advantages, including the ability to upscale laboratory research into commercially viable processes. Through the software's design capabilities, equipment costs, as well as material and energy input/output flows, can be reliably determined. Subsequently, these input/output data and associated costs were used to obtain both the capital and operating costs required for the integrated TEA. Furthermore, the material and energy input/output flows, identified through

Aspen Plus simulations, were integrated into the LCA to gain insight into environmental impact. The existing process model from Sproul, et al. [47] developed through Microsoft Excel, was updated by integrating the results of both the TEA and LCA from the resin co-products to determine an updated MRSP.

Low-Molecular-Weight Rubber Separation

A solvent-based guayule processing facility was modeled to generate three distinct output streams: (high-molecular weight) rubber, bagasse, and a resin/LMWR mixture [10]. The extraction of LMWR, *cis*-1,4-polyisoprene, from the resin is required before converting the resin stream into valuable co-products. The process model for LMWR separation via acetone washing is based upon data from Schloman et al. [44].

Material components and thermodynamic methods were first defined to create the simulation in Aspen Plus, using resin characterization data from Dehghanizadeh et al. [61]. Due to the complex composition of the resin, only mass fractions of ~1% or greater were used. Guayulins and argentatins do not exist in the Aspen Plus molecule database so they were manually defined as non-conventional components using the Molecule Editor tool. Polyisoprene was used for LMWR and the polymer non-random two-liquid (POLY-NRTL) thermodynamic model was selected due to its suitability for non-ideal systems containing polymers.

The simulation design was initiated by creating a feed stream with predetermined mass fractions, temperature, pressure, and flow rate. The feed flow rate of 2757 kg/h of resin/LMWR mixture was based on a process model for a natural rubber processing facility in Pinal County, AZ (Sproul et al., 2020). Three separator units facilitated the washing of LMWR from the resin. Each separator had two entering feed streams: the LMWR/resin mixture and acetone, and two exiting product streams: the LMWR/acetone wash and the residual resin. The retentions of LMWR in the resin products from first, second, and third separators were 15%, 3%, and 0% respectively. The three product streams containing LMWR solute in acetone were combined to obtain the final product stream of LMWR; the acetone was subsequently separated from the LMWR and recycled back into the system assuming a 2% solvent loss [6]. The obtained LMWR was mixed with any residual resin from each of the three co-products pathways to form an asphalt binder. The overall design of the simulation can be found in Figure A - 1.

Essential Oils Pathway Process Model

Guayule resin contains a class of volatile compounds called monoterpenes [10]. Alpha-pinene is the primary monoterpene present, with beta-pinene and d-limonene representing a notable fraction of the other monoterpenes. These can be isolated from the resin and used in production of essential oils, which are widely utilized as fragrance and flavor additives in cosmetics, residential cleaning products, foods, and textiles [3].

The isolation of monoterpenes from the residual resin stream was achieved through benchtop vacuum distillation, which was carried out experimentally in an environmental control chamber at pressures as low as 414 Pa. Vacuum distillation is a well-established technique for separating essential oils involving distillation of liquids under reduced pressure [59].

As with the LMWR separation process model, material components and thermodynamics were first defined in Aspen Plus. The feed stream was comprised of the effluent stream from the LMWR removal simulation. The universal quasichemical functional group activity coefficient (UNIFAC) method was employed as the thermodynamic method. UNIFAC is a binary parameter interaction estimator that is particularly useful in the initial stages of physical property data investigation [11].

To separate an *n*-component mixture, the ideal distillation configuration is to use exactly *n*-1 columns [24]. Three distillation columns were chosen for the model. Packed columns were chosen over trays due to their ability to provide a more uniform distribution of vapor and liquid throughout the column [37]. Metal was selected as the packing material due to its ability to handle extreme pressures [38].

Initially, a simplified distillation model (DWTSU) was designed to obtain the required number of stages, reflux ratio, and heat duties. The DWTSU design served as the foundation for a more rigorous distillation column, RADFRAC. The RADFRAC was put through further iterations and optimizations to yield the final results (Figure A - 2).

The feed stream was heated to 134°C and the pressure adjusted to 620 Pa before entering the first column. Monoterpenes were distilled off as the top product, with residual resin as the bottom product. The second distillation column had the three monoterpenes entering, with d-limonene as the bottom product and the two pinenes as the distillate. The final distillation column involved the separation of alpha-pinene (tops) from beta-pinene (bottoms). Table A - 1**Error! Reference source not found.** in the appendix provides a detailed overview of the parameters for the three distillation columns. The product streams leaving the system had a combined flow rate of 136 kg/h, with alpha-pinene, beta-pinene, and d-limonene purities of 98%, 97%, and 99%, respectively.

Insect Repellant Pathway Process Model

The mono- and sesquiterpenes, and their oxygenated derivatives, in the guayule resin are among active insect-repellent compounds identified in the literature [27]. A recent study by Dehghanizadeh et al. (in review) tested the vacuum-distilled fractions from guayule resin against Turkestan cockroaches (*Blatta lateralis* Walker). All the fractions performed well in their fresh form (tested approximately 20 min after application); the best-performing fractions were the heavier vacuum-distilled fractions that are rich in oxygenated sesquiterpenes and lipids. The lipids act as an encapsulating agent and control the release of active compounds (such as alpha-eudesmol), giving rise to longer action time (more than 7 days) (Dehghanizadeh et al. in review).

A process model for the commercial production of insect repellant active ingredient from guayule resin was created in Aspen Plus using a single vacuum distillation column. UNIFAC was again chosen as the thermodynamic method. The input steam components were defined from the effluent stream of the LMWR model. Prior to entering the distillation column, the feed stream was heated to 160°C and the pressure adjusted to 1380 Pa. The distillation column produced a total of five product streams (designated as fractions B-J in the experimental study), four of the product streams comprising fractions B-F and the other comprising fractions G-J. The most active insect-repellent co-product was shown (Dehghanizadeh et al., in review) to be present in fractions G, H, I, and J, which accounted for 20% of the mass fraction. The remaining 80% of residual resin, fractions B-F, was mixed with the LMWR to produce an asphalt binder as a secondary co-product. The Aspen Plus process model diagram is shown as Figure A - 3.

Resin-Urea Formaldehyde Blend Adhesive Pathway Process Model

Bench experiments have shown that UF resin can be combined with significant amounts of guayule resin, devoid of LMWR, while still maintaining strength and adhesiveness comparable to that of pure UF resin. These bench experiments served as a basis for an Aspen Plus simulation for the resin blend adhesive co-product. The Aspen simulation feed stream was comprised of the effluent stream of the LMWR removal simulation, as well as acetone and UF powder. The UF powder was represented in the components separately as urea and formaldehyde. The thermodynamic method used was NRTL, which is suitable for non-ideal multicomponent liquid mixtures [57].

Initially, acetone was mixed with guayule resin at a ratio of 1 ml to 1 g. The resulting blend was then fed into a continuous stirred-tank reactor (CSTR) and allowed to mix for 2 h at 10 psia (69 kPa) and 29°C. The effluent from the first CSTR, containing the resin/acetone blend, was combined with water and UF powder in a second CSTR. The mixture was allowed to mix for 1 h at 10 psia (69 kPa) and 29°C, which resulted in a final product of guayule resin-UF blend adhesive.

The final product stream consisted of 85% resin/acetone blend, 8.4% UF powder, and 6.6% water. These mass fractions were chosen as there was no significant difference in adhesion strength compared to UF up to an 85% resin blend (Figure A - 4). The Aspen Plus process model diagram for this process is shown as Figure A - 5.

Techno-economic Analysis

The economic evaluation of each resin co-product pathway was conducted using TEA methodology. Capital and operating costs were derived from Aspen Plus process models using

Aspen Economic Analyzer. Capital costs encompassed the costs of purchased equipment, design, engineering, and construction required for the co-product separation processes. Operating costs encompassed utilities, material inputs, labor, benefits, maintenance, and insurance. The utility costs outlined in Sproul et al. [47] were utilized to determine the expenses associated with material and energy inputs (Table A - 2**Error! Reference source not found.**). All costs and co-product revenues associated with each of the three resin co-products were integrated into the process model for a natural rubber biorefinery situated in Pinal County, AZ, with guayule bagasse sold at $0.10 per kg [47]. The selling price of the essential oil co-product was established by using individual monoterpene price data from literature and calculating an average product selling price from the mass fractions of the three monoterpenes [53, 48, 46]. The selling price of the insect repellant co-product was determined by analyzing active ingredients of nine distinct commercially available bio-based cockroach repellants and identifying the selling price for the active ingredients. The selling price of the resin blend adhesive product was taken from relevant literature [60] and further validated through comparison against a phenol formaldehyde market report [30]. A discounted cash flow rate of return analysis was applied to determine the MRSP of guayule that would result in a net present value of zero after a 30-year operating lifetime. Additional economic input parameters for the TEA process model are shown in Table A - 3.

Life-Cycle Assessment

Using a cradle-to-gate LCA methodology set out by the International Organization for Standardization [20, 21], an environmental analysis was carried out in a similar manner as the TEA. Each of the three resin co-product pathways system boundaries started from the preparation of the land for guayule planting and extended through the production of the guayule rubber, bagasse, and resin co-product. Emissions data were sourced from Ecoinvent 3.9 and the United States Life Cycle Inventory Database [64]. Consistent with standard LCA cut-off methodologies, the environmental impacts associated with capital infrastructure materials (such as steel and concrete) were excluded from this study due to their negligible effect when allocated over the 30-year operational period [20, 21]. The cumulative emissions stemming from guayule rubber production were quantified via GWP using the U.S. Environmental Protection Agency Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) version 2.1 [7]. The resin was assumed to not include any embodied emissions and to come into the system burden free.

Four forms of allocation were utilized to present four different perspectives since allocation can both isolate the impact of individual products and produce substantial changes in results, ultimately leading to different conclusions. The first method combined economic and displacement allocation. The second method combined mass and displacement allocation. The third method used mass allocation, distributing the environmental impacts among products based on their overall mass. The fourth method used economic allocation, distributing the environmental impacts based on the economic value of each product. In displacement allocation, the environmental impact associated with product production is offset by production of an equivalent product, leading to an environmental impact subtracted [23]. Once the subtraction has been allocated to the system as a whole, a mass allocation and market allocation were subsequentially performed. These allocations were then compared to the baseline guayule natural rubber facility impacts in the integrated analysis.

Sensitivity Analysis

A sensitivity analysis was conducted to identify the individual input parameters that have the greatest impact on the economic and environmental results. Each input parameter was varied individually by ± 20%, and a new MRSP and GWP were generated. The parameters with the highest impact on the results were then identified, highlighting which inputs were most sensitive to changes in uncertainty.

CHAPTER 3: RESULTS & DISCUSSION

The results are presented in three main parts. First, the outcomes from the Aspen Plus process model simulations for each of the resin co-product pathways are presented with detailed energy and mass balances and economic costs. Next, the results from the integration into the guayule biorefining model show the systems level economic and environmental impact of each co-product pathway on the produced natural rubber. Finally, the integrated guayule-based biorefinery concepts are compared to that of hevea rubber. This comparative analysis enables a thorough evaluation of the relative performance and viability of guayule resin co-products in relation to the broader natural rubber industry.

Aspen Plus Simulation Results

The Aspen Plus simulation results are broken into four sections, corresponding to the removal of LMWR and the three resin co-product pathways. Summaries of the economic results and environmental results are presented in **Error! Reference source not found.** and * *Range in values contingent on downstream resin pathway*

The contributions of various factors to GWP in each of the three resin co-product pathways is illustrated in **Error! Not a valid bookmark self-reference.**. Notably, the largest impact of GWP is the utilization of natural gas observed in both the essential oil and insect repellent pathways. The reliance on natural gas for distillation columns and heaters in these pathways contributes to the substantial environmental impact. In contrast, the resin blend adhesive pathway demonstrates a significantly lower GWP. This is attributed to the absence of heaters or distillation columns during the co-product production process. Although natural gas has a substantial influence of GWP, acetone, despite having a relatively smaller impact, emerges as the largest contributor within the resin blend adhesive pathway.

In the context of mass allocation, the annual impact is divided by the annual production rate on a per kilogram basis. The results are then normalized based on the yield out of the system, and subsequently the resin blend adhesive pathway will have a considerably lower impact than the other two pathways due to its high yield. This higher yield (147% of the resin) is due to the addition of acetone, water, and UF powder to the resin. In the essential oil pathway, only approximately 5% of the resin is converted into the essential oil co-product, while in the insect repellent pathway, about 20% of the resin is converted into the insect repellent co-product. Consequently, the mass allocation approach reveals that the GWP impact of the insect repellent pathway is lower than that of the essential oil pathway. Considering both the annual environmental impact and mass allocation, the resin blend adhesive pathway emerges as the most favorable option. It not only exhibits lower annual impacts but also demonstrates reduced environmental impact when evaluated on a per kilogram basis.

Table 2, respectively.

Low-molecular weight rubber yield, economic and environmental analysis

The LMWR accounts for 30% of the total mass fraction of the resin, corresponding to a production rate of 19.8 tonnes/day. A summary of the simulation stream results is shown in Figure A - 6. The estimated total capital cost is $2.33 million, with the separators contributing 100% to equipment costs (Table A - 4). The total operational costs are $1.87 million, with variable operating costs accounting for 48% and fixed operating costs accounting for the remaining 52%. The purchase of acetone is the largest contributor to the variable operating costs. The selling price of the asphalt binder is $270 per tonne, with the annual U.S. market size estimated at 26.6 million metric tons in 2020, indicating no concern for market saturation [1]. A sensitivity analysis is not performed as LMWR removal is a required pre-processing step for the three resin co-product pathways.

The total life cycle impact of LMWR removal and the relative contributions of different operations is displayed in * *Range in values contingent on downstream resin pathway*

The contributions of various factors to GWP in each of the three resin co-product pathways is illustrated in **Error! Not a valid bookmark self-reference.**. Notably, the largest impact of GWP is the utilization of natural gas observed in both the essential oil and insect repellent pathways. The reliance on natural gas for distillation columns and heaters in these pathways contributes to the substantial environmental impact. In contrast, the resin blend adhesive pathway demonstrates a significantly lower GWP. This is attributed to the absence of heaters or distillation columns during the co-product production process. Although natural gas has a substantial influence of GWP, acetone, despite having a relatively smaller impact, emerges as the largest contributor within the resin blend adhesive pathway.

In the context of mass allocation, the annual impact is divided by the annual production rate on a per kilogram basis. The results are then normalized based on the yield out of the system, and subsequently the resin blend adhesive pathway will have a considerably lower impact than the other two pathways due to its high yield. This higher yield (147% of the resin) is due to the addition of acetone, water, and UF powder to the resin. In the essential oil pathway, only approximately 5% of the resin is converted into the essential oil co-product, while in the insect repellent pathway, about 20% of the resin is converted into the insect repellent co-product.

Consequently, the mass allocation approach reveals that the GWP impact of the insect repellent pathway is lower than that of the essential oil pathway. Considering both the annual environmental impact and mass allocation, the resin blend adhesive pathway emerges as the most favorable option. It not only exhibits lower annual impacts but also demonstrates reduced environmental impact when evaluated on a per kilogram basis.

Table 2. The largest contributor is the acetone required for the start-up of the operation. The impact of electricity on the entire process is low. The resulting total GWP for LMWR removal only (mass allocation excluding upstream operations and resin co-product production) is 4.35E-01 kg CO_2 per kg LMWR. The LMWR removal process exhibits a similar environmental impact to mastic asphalt production, its traditional displaced product once converted into asphalt binder, whose GWP is measured at 2.42E-01 kg CO_2 per kg mastic asphalt. The results suggest that the LMWR removal process can offer a sustainable solution to the traditional mastic asphalt binder while maintaining a comparable environmental footprint.

Essential oils yield, economic and environmental analysis

Essential oil products accounted for 4.9% of the total mass fraction of the resin, consisting of 3.6% alpha-pinene (2.35 tonnes/day; 97% purity), 0.74% beta-pinene (0.491 tonnes/day; 98% purity), and 0.64% d-limonene (0.426 tonnes/day; 99% purity) (Figure A - 7). The total estimated capital cost is $5.87 million, with the distillation columns contributing 88% to the equipment costs (Table A - 5). The total operational costs amounted to $5.84 million, with variable operating costs accounting for 75% and fixed operating costs accounting for the remaining 25%. The use of natural gas required for heating and pressurizing the feed stream prior to entering the first distillation column is the largest contributor to the variable operating costs. The selling price of the essential oil co-product is $5.80 per kg [46, 48, 53, 58], with an annual U.S. market size estimated at $3.00 billion USD in 2021 [18], indicating no concern for market saturation. Results from the TEA sensitivity analysis (Figure A - 8) reveal that the co-product price and operating cost have the highest impact on the MRSP. Co-product price and operating cost directly affect the revenue associated with the essential oil pathway, leading to a direct impact on MRSP when evaluated on a biorefinery level.

The total life cycle impact of the essential oil co-product and the relative contributions of different operations are shown in * *Range in values contingent on downstream resin pathway*

The contributions of various factors to GWP in each of the three resin co-product pathways is illustrated in **Error! Not a valid bookmark self-reference.**. Notably, the largest impact of GWP is the utilization of natural gas observed in both the essential oil and insect repellent pathways. The reliance on natural gas for distillation columns and heaters in these pathways contributes to the substantial environmental impact. In contrast, the resin blend adhesive pathway demonstrates a significantly lower GWP. This is attributed to the absence of heaters or distillation columns during the co-product production process. Although natural gas has a substantial influence of GWP, acetone, despite having a relatively smaller impact, emerges as the largest contributor within the resin blend adhesive pathway.

In the context of mass allocation, the annual impact is divided by the annual production rate on a per kilogram basis. The results are then normalized based on the yield out of the system, and subsequently the resin blend adhesive pathway will have a considerably lower impact than the other two pathways due to its high yield. This higher yield (147% of the resin) is due to the addition of acetone, water, and UF powder to the resin. In the essential oil pathway, only approximately 5% of the resin is converted into the essential oil co-product, while in the insect repellent pathway, about 20% of the resin is converted into the insect repellent co-product.

Consequently, the mass allocation approach reveals that the GWP impact of the insect repellent pathway is lower than that of the essential oil pathway. Considering both the annual environmental impact and mass allocation, the resin blend adhesive pathway emerges as the most favorable option. It not only exhibits lower annual impacts but also demonstrates reduced environmental impact when evaluated on a per kilogram basis.

Table 2. The largest contributor is the natural gas required for the operation. The impacts of water and electricity on the entire process are low. Sensitivity analysis on GWP (Figure A - 9) showed that the total emissions are primarily affected by the natural gas required, more specifically, for the medium pressure steam (MPS). The resulting total GWP for the essential oils (mass allocation excluding upstream operations and asphalt binder production) is 1.16E+06 kg CO_2 per kg essential oil. Essential oil production exhibits a significantly higher environmental impact than mint production, which is assumed to be displaced in this study. Mint production is chosen as the traditional for product as it most closely resembles the production for essential oils. The GWP impact of mint production is measured at 0.811E-02 kg CO_2 per kg mint [64]. The guayule resin essential oil pathway is unfavorable from an environmental perspective given its higher GWP impact with the value reported here being a conservative estimate.

Insect repellant yield, economic and environmental analysis

Insect repellant accounts for 20% of the total mass fraction of the resin corresponding to a production rate of 13.2 tonnes/day (Figure A - 10). The estimated total capital cost is $2.90 million, with the distillation column contributing 63% to the equipment costs (Table A - 6). The total operational costs are $4.66 million, with variable operating costs accounting for 79% of the total costs and fixed operating costs accounting for the remaining 21%. Similar to the essential oil co-product pathway model, the use of natural gas for heating and pressurizing the feed stream prior to entering the distillation column is the largest contributor to the variable operating costs.

The selling price of the insect repellant co-product is $41.40 per kg (Table A - 7) when the production rate of insect repellant from a guayule rubber biorefinery is 4.63 million kg annually. This production rate represents 445% of the annual market size., with an annual U.S. market size estimated at 1.04 million kg [5, 62, 63], indicating significant concern for market saturation. If 25% of the current market is assumed to be reached, only 5.7% of the insect repellant produced from guayule resin would be sold. The TEA sensitivity analysis (Figure A - 11) showed that co-product price and market share have the highest impact on the MRSP. The biorefinery's performance is highly sensitive to small price fluctuations and small adjustments in the market share capture will significantly impact the overall sensitivity of the system.

The total life cycle impacts of the insect repellant co-product and the relative contributions of different operations are shown in * Range *in values contingent on downstream resin pathway*

The contributions of various factors to GWP in each of the three resin co-product pathways is illustrated in **Error! Not a valid bookmark self-reference.**. Notably, the largest impact of GWP is the utilization of natural gas observed in both the essential oil and insect repellent pathways. The reliance on natural gas for distillation columns and heaters in these pathways contributes to the substantial environmental impact. In contrast, the resin blend adhesive pathway demonstrates a significantly lower GWP. This is attributed to the absence of heaters or distillation columns during the co-product production process. Although natural gas has a substantial influence of GWP, acetone, despite having a relatively smaller impact, emerges as the largest contributor within the resin blend adhesive pathway.

In the context of mass allocation, the annual impact is divided by the annual production rate on a per kilogram basis. The results are then normalized based on the yield out of the system, and subsequently the resin blend adhesive pathway will have a considerably lower impact than the other two pathways due to its high yield. This higher yield (147% of the resin) is due to the addition of acetone, water, and UF powder to the resin. In the essential oil pathway, only approximately 5% of the resin is converted into the essential oil co-product, while in the insect repellent pathway, about 20% of the resin is converted into the insect repellent co-product. Consequently, the mass allocation approach reveals that the GWP impact of the insect repellent pathway is lower than that of the essential oil pathway. Considering both the annual environmental impact and mass allocation, the resin blend adhesive pathway emerges as the most favorable option. It not only exhibits lower annual impacts but also demonstrates reduced environmental impact when evaluated on a per kilogram basis.

Table 2. The largest contributor is the natural gas required for the operation. The impacts of water and electricity on the entire process are low. Results from the sensitivity analysis on GWP (Figure A - 12) showed that total emissions are primarily affected by the resin extraction process. The resulting total GWP for insect repellant (mass allocation excluding upstream operations and asphalt binder production) is 2.55E+04 kg CO_2 per kg insect repellant. Insect repellent production exhibits a significantly higher environmental impact than pesticide, its traditional displaced product, whose GWP is measured at 1.13E+01 kg CO_2 per kg pesticide. The guayule resin insect repellent pathway is unfavorable from an environmental perspective given its higher GWP impact.

Resin blend adhesive yield, economic and environmental analysis

Resin blend adhesive accounts for 147% of the total mass fraction of the resin, corresponding to a production rate of 97.5 tonnes/day (see CSTR blend simulation results in Figure A - 13). This high percentage is achieved through the addition of acetone, water, and UF powder to the original resin stream. The total estimated capital cost is $2.62 million, with the initial CSTR contributing 57% to the equipment costs (Table A - 8**Error! Reference source not found.**). The total operational costs are $14.2 million, with variable operating costs accounting for 91% of the total and fixed operating costs accounting for the remaining 9%. Acetone and UF powder are the largest contributors to the variable operating costs. The selling price of the resin blend adhesive co-product is $2.50 per kg [30, 60], with an annual North American market estimated at $2.80 billion in 2020 [30], indicating no concern for market saturation. The TEA sensitivity analysis (Figure A - 14) showed that the co-product price has the highest impact on the MRSP. The resin blend adhesive co-product contributes significantly to the overall revenue of a natural rubber biorefinery, small variations in the prices can have a substantial impact on the biorefinery's performance.

The total life cycle impact of the resin blend adhesive co-product and the relative contributions of different operations are shown in * *Range in values contingent on downstream resin pathway*

The contributions of various factors to GWP in each of the three resin co-product pathways is illustrated in **Error! Not a valid bookmark self-reference.**. Notably, the largest impact of GWP is the utilization of natural gas observed in both the essential oil and insect repellent pathways. The reliance on natural gas for distillation columns and heaters in these pathways contributes to the substantial environmental impact. In contrast, the resin blend adhesive pathway demonstrates a significantly lower GWP. This is attributed to the absence of heaters or distillation columns during the co-product production process. Although natural gas has a substantial influence of GWP, acetone, despite having a relatively smaller impact, emerges as the largest contributor within the resin blend adhesive pathway.

In the context of mass allocation, the annual impact is divided by the annual production rate on a per kilogram basis. The results are then normalized based on the yield out of the system, and subsequently the resin blend adhesive pathway will have a considerably lower impact than the other two pathways due to its high yield. This higher yield (147% of the resin) is due to the addition of acetone, water, and UF powder to the resin. In the essential oil pathway, only approximately 5% of the resin is converted into the essential oil co-product, while in the insect repellent pathway, about 20% of the resin is converted into the insect repellent co-product. Consequently, the mass allocation approach reveals that the GWP impact of the insect repellent pathway is lower than that of the essential oil pathway. Considering both the annual environmental impact and mass allocation, the resin blend adhesive pathway emerges as the most favorable option. It not only exhibits lower annual impacts but also demonstrates reduced environmental impact when evaluated on a per kilogram basis.

Table 2. The largest contributors are the acetone and UF powder required for the operation. The impacts of water and electricity on the entire process are low. Results from the sensitivity analysis GWP (Figure A - 15) showed that the total emissions are primarily affected by the co-product yield and the acetone flow rate. The resulting total GWP for resin blend adhesive (mass allocation excluding upstream operations and asphalt binder production) is 9.93E-01 kg CO_2 per kg resin blend adhesive. Resin blend adhesive production exhibits a significantly higher environmental impact than UF resin, its traditional displaced product, whose GWP is measured at 3.32E+00 kg CO_2 per kg UF resin. Unlike the other two pathways, the

guayule resin blend adhesive pathway is favorable from an environmental perspective given its lower GWP impact.

Economic and Environmental Comparison of the Three Resin Co-product Pathways

An economic overview of the three resin pathways is presented in **Error! Not a valid bookmark self-reference.**. Among these pathways, the essential oil pathway incurs the highest capital costs. This can be attributed to the substantial expenses associated with the acquisition of distillation columns. In contrast, the insect repellent pathway requires only a single distillation column, while the resin blend adhesive pathway does not require any distillation equipment. Consequently, the capital costs of these pathways align with their respective distillation needs. When considering the operating costs, the resin blend adhesive pathway emerges as the costliest among the three. This is primarily due to the expense involved in procuring non-recycled acetone and UF powder, both of which are essential materials for this pathway.

The insect repellent pathway, despite demonstrating a higher product price, has limitations on the quantity of product that is sold due to the constrained market size. Consequently, the insect repellent pathway fails to generate product sales proportionate to its elevated product price. In contrast, the resin blend adhesive pathway, despite offering the lowest product price, emerges as the most profitable option for a natural rubber biorefinery. This favorable outcome is primarily attributed to the large market size and substantial production rate resulting from increasing resin yield. Accordingly, the resin blend adhesive pathway generates the highest sales volume among the three pathways, making it a favorable choice for natural rubber biorefineries from a financial standpoint.

Table 1: Techno-economic results for the three potential resin co-product pathway & Asphalt Binder.

Parameter	**Asphalt Binder (Low-molecular Weight Rubber & Residual Resin)**	**Essential Oils**	**Insect Repellant**	**Resin Blend Adhesive**
Capital costs (MM USD)	2.32-2.33*	5.87	2.90	2.62
Operating costs (MM USD)	1.87-1.90*	5.84	4.77	14.2
Production rate (kilotonnes/yr)	6.95-22.0*	1.14	4.63	34.1
Product selling price (USD/kg)	0.270	5.70	41.4	2.50
Product market size	2.6 billion kgs	$3.0 billion	4.6 million kgs	$2.8 million
% Of product sold	100%	100	5.70	100
Product Sales (MM USD/yr)	1.88-5.95*	6.77	10.8	119

* *Range in values contingent on downstream resin pathway*

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Table 2: Greenhouse gas environmental impact contributions (kg CO2 eq per year and per kg product) to each resin co-product pathway.

	Low-molecular Weight Rubber Removal	**Essential Oils**	**Insect Repellant**	**Resin Blend Adhesive**
Water	-	1.13E+02	7.85E+03	2.99E+02
Electricity	2.17E+05	4.27E+06	2.18E+05	5.27E+05
Electricity (Asphalt Binder Mixing)	-	2.55E+05	2.55E+05	-
Natural Gas	-	1.33E+11	1.18E+11	-
Acetone	2.81E+06	-	-	2.85E+07
Urea Formaldehyde Powder	-	-	-	4.86E+06
Total (kg CO_2 eq annually)	3.02E+06	1.33E+11	1.18E+11	3.39E+07
Total (kg CO_2 eq per kg product)	0.435	1.16E+06	2.55E+04	0.993

Integrated Economics and Environmental Findings for a Guayule Biorefinery

An existing baseline process model developed by Sproul et. al [47] for a guayule natural rubber facility in Pinal County, AZ, operates on the assumption that the co-products, bagasse and resin, can be sold at prices of $0.10 per kg and $1.00 per kg, respectively, resulting in a MRSP of $3.05 per kg. The sale price of resin at $1.00 per kg remains an unknown variable in the model. By integrating the economic outcomes of the three separate resin co-product pathways, a more accurate estimate of the actual value of the resin is possible. Guayule co-products that meet or surpass the assumed value of $1.00 per kg of resin have the potential to significantly reduce the MRSP, making guayule rubber more competitive with hevea rubber, which has a market price of $2.02 per kg as of April 2023 [42].

The economic results of the baseline and three resin co-product scenarios are shown in **Error! Reference source not found.**. The baseline case (from Sproul et al. [47]) has an MRSP o f $3.05 per kg. The MRSP are $3.54 per kg, $3.40 per kg, and $1.69 per kg for the essential oil, insect repellent and adhesive pathways, respectively. The baseline pathway does not include removal of LMWR, nor the sale of combined LMWR and any residual resin fractions as an asphalt binder co-product. The resin blend adhesive generates the most revenue for a guayule production facility when compared to the other two co-products and stands out as the most promising pathway forward to improve the commercial viability of a guayule biorefinery.

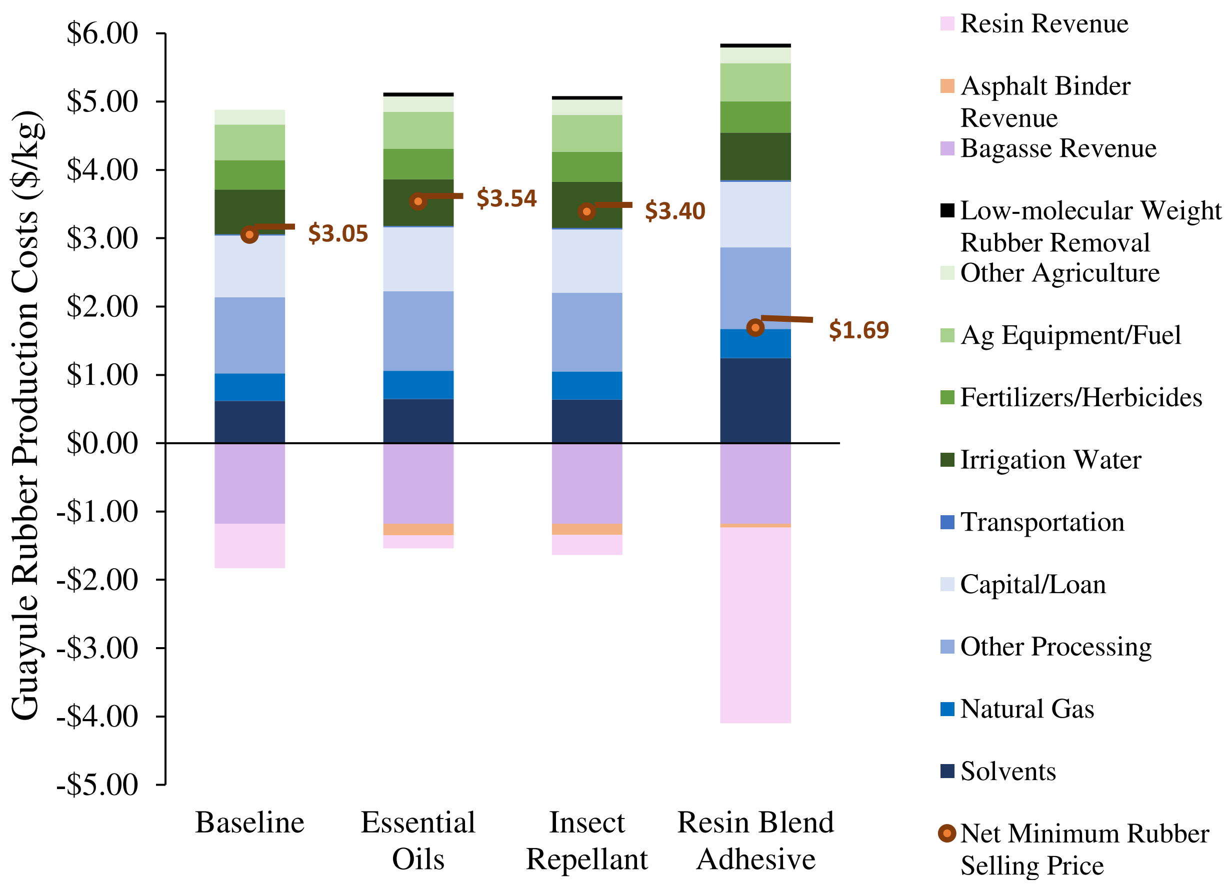

*Figure 2: **Guayule** minimum rubber selling price (MRSP) necessary for a net present value of zero over 30 years of production. The costs of production are categorized into agriculture (green), transportation (yellow), and co-product extraction (blue). The baseline scenario features co-product revenues of $1.00 per kg of resin (pink) and $0.10 per kg of bagasse (purple). The three resin pathway scenarios use co-product revenues of $0.10 per kg of bagasse (purple), $0.27 per kg of asphalt binder (orange), and $5.70, $41.40, and $2.50 per kg for essential oils, insect repellant, and resin blend adhesive resin co-products (pink), respectively.*

The total GWP impacts from the baseline and three resin co-product pathways (agriculture, transportation, and biorefining) are presented in **Error! Reference source not found.**. In the baseline scenario, the overall impacts are allocated to rubber, bagasse, and resin using mass and economic allocations. To evaluate the impact of the three resin co-product scenarios, hybrid approaches combining displacement allocation with either mass or economic allocation are performed considering the market displacement of mint production as a proxy for the essential oils, pesticide production, and UF adhesive production.

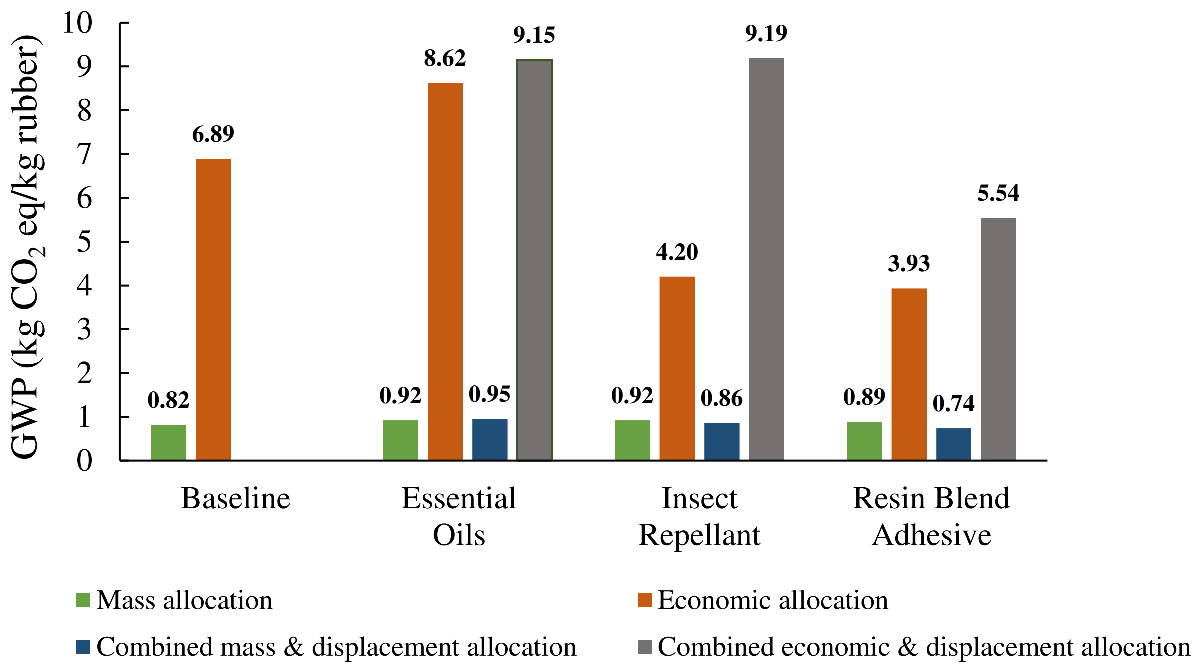

Figure 3: Global warming potential comparison of the baseline and three resin co-product scenarios using mass (green) allocation, economic (orange) allocation, combined displacement and mass (blue) allocation, and combined displacement and economic (gray) allocation. Results are displayed on a carbon dioxide equivalence (CO2 eq).

The choice of allocation method significantly impacts the distribution of emissions within a natural rubber biorefinery (**Error! Reference source not found.**). The mass allocation a pproach leads to a biased assessment as the bagasse, with a considerably higher mass contribution (80-90%) compared to rubber (5-10%) and resin (5-10%), receiving a disproportionate share of the impacts. Mass allocation fails to account for the economic importance of each co-product. Given that the rubber primary product commands higher market demand and pricing, a more accurate allocation of environmental impacts is warranted. While the economic allocation method provides a more accurate and equitable approach within a natural rubber biorefinery, it neglects to consider market volatility such as market saturation or supply chain impact. A hybrid approach integrating both economic and displacement methods is performed in an effort to effectively estimate the environmental impact of the products. Initially, the environmental impact of replacing existing traditional products on the market is subtracted from the system (displacement method), based on the respective resin co-product pathways. Subsequently, an economic allocation is performed by allocating this updated environmental impact to the specific products based on their market share. Only the guayule co-products that do not displace traditional products on the market, rubber and bagasse, are assigned environmental impact. This approach captures both the physical and economic aspects of the system, specifically in the context of a guayule natural rubber biorefinery. This approach effectively deals with the issue of the bagasse having a large mass fraction but low economic value.

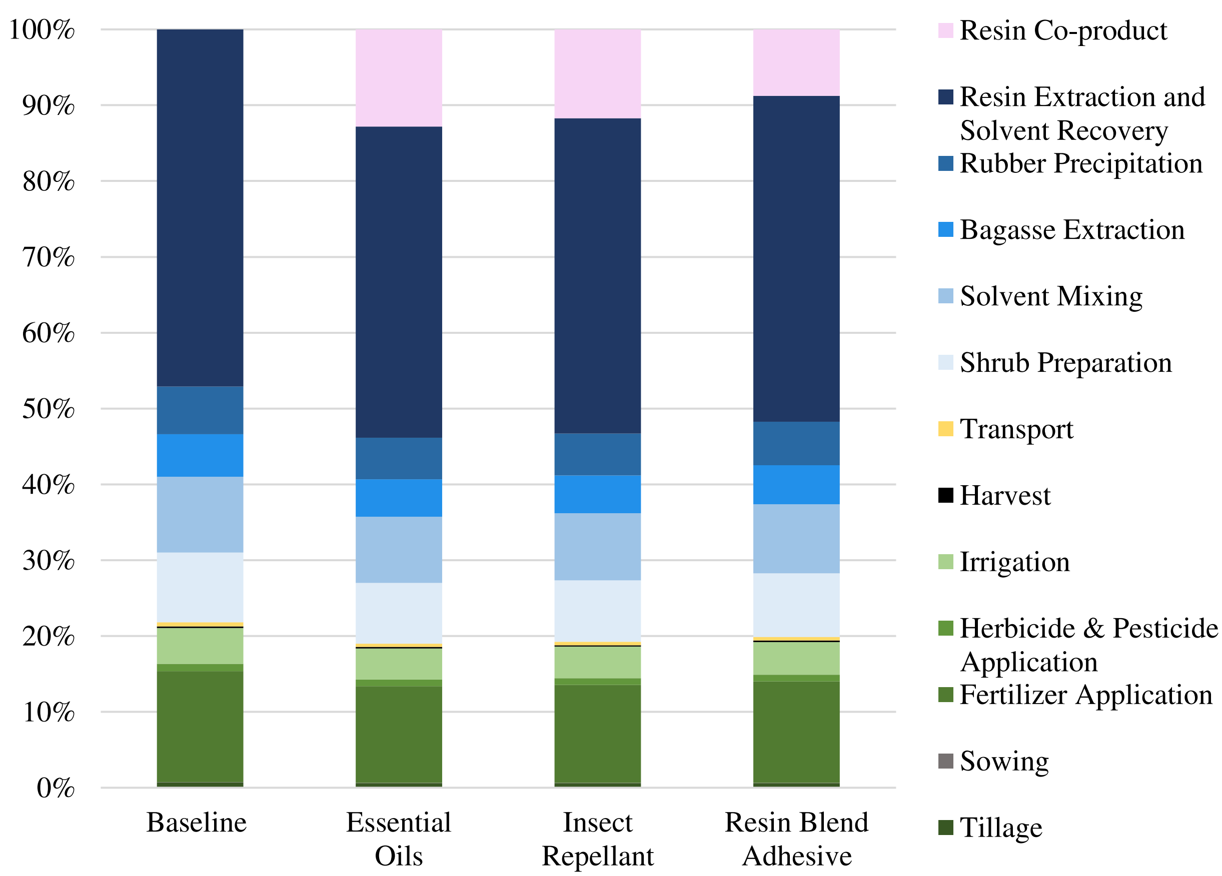

Figure 4: The global warming contributions per kg rubber by process steps for the baseline and three resin co-product scenarios broken out by agriculture (green), transportation (yellow), rubber extraction (blue), and resin co-product formation (pink).

The GWP contributions of the activities for the baseline scenario and three resin co-product scenarios are illustrated in Figure 4, categorized into agriculture, transportation, rubber extraction, and resin co-product formation. The production of essential oil accounts for 13% of the total environmental impact. Within essential oil production, the greatest overall impact is attributed to the use of natural gas for the heater to heat the feed stream from 29.4°C to 135°C and for the distillation column reboilers. The production of insect repellent accounts for 12% of the total environmental impact; the impact is also closely linked to the energy-intensive heating processes that use natural gas. Despite having only one column reboiler, compared to the essential oil pathway's three reboilers, the feed stream in the insect repellent pathway requires heating from 29.4°C to 160°C, resulting in higher natural gas consumption. The production of resin blend adhesive accounts for 9% of the total environmental impact. Acetone and UF powder are responsible for the largest overall impacts despite the absence of natural gas usage for heating. Ultimately, the resin blend adhesive pathway exhibits the least environmental impact in a guayule natural rubber biorefinery due to the lack of natural gas usage when considering the entire life cycle.

The resin blend adhesive produces 34.1 E+03 tonnes of product per year with an associated annual revenue of $85.3 million. In comparison, a guayule natural rubber biorefinery produces 35.6 E+03 tonnes of product per year, resulting in a yearly revenue of $60.2 million. Selecting the resin blend adhesive as the primary resin pathway raising the question of whether guayule production facilities should emphasize the yield of the resin blend adhesive co-product and invest in new technology or equipment for this co-product or continue to focus on guayule rubber production to meet demand and maximize revenue.

Economic and Environmental Comparison to Hevea Rubber

Hevea rubber currently dominates the global natural rubber supply, comprising more than 90% of the market [28]. To enhance the relative competitiveness of guayule, the value of the resin co-product needs to be enhanced to decrease the price of guayule rubber [10]. The integrated analysis shows that the resin blend adhesive pathway has a significant effect on the selling price of rubber compared to the current market values of two types of hevea rubber, technically specified rubber (TSR20) and ribbed smoked sheets (RSS3). Monthly market price distributions from May 2013 to May 2023 shows values ranging from \$1.38 per kg to \$3.80 per kg, with a median price of \$2.04 per kg and \$2.44 per kg for TSR20 and RSS3, respectively. The MRSP of guayule, when choosing resin blend adhesive as the resin pathway, is \$1.69 per kg. This value is within the inner 50th percentile of hevea market prices from the past ten years, making guayule a cost-competitive alternative [42, 43]. The other co-product pathways, essential oils and insect repellent, are shown to be outside the 50th percentile of hevea market prices from the past 10 years.

Production of guayule in the southwestern U.S. as an alternative to hevea rubber necessitates a close comparison of the environmental impacts of the two natural rubber product systems. A cradle-to-gate life cycle assessment on hevea rubber manufactured in Liberia showed that, through mass allocation, 1 kg of hevea block rubber emits 0.36 kg CO_2 eq (Antonanzas et al., in review). Guayule is currently modeled to emit 0.66-0.95 kg CO_2 eq per kg rubber, indicating that hevea rubber has a smaller impact on the environment. This lower level of emissions is attributed to the rudimentary process of tapping sap from trees, which is largely performed by small local farmers in southeast Asia. That LCA did not account for any land-use changes associated with converting rainforests into hevea tree farms, which could be a factor as natural rubber demand increases. Currently, global demand for natural rubber is increasing at a 3.5% compound annual growth rate [17]. A recent first-order estimate calculated that the carbon footprint of hevea rubber with land use change would be 34 kg CO_2 eq per kg rubber (Antonanzas, under review manuscript), significantly higher than guayule's environmental footprint. This indicates the potential for guayule rubber to meet future natural rubber demand more sustainably.

Future Work

Among the potential guayule resin biorefinery options, production of bio-based cockroach repellent alone is not economically feasible. Expanding repellent/anti-feedant applications to other pests, like mosquitoes and other flying insects, or to building materials and textiles, may increase the market size enough to pursue that resin pathway. As the demand for non-toxic products continues to grow, the market for bio-based insect repellants is likely to expand and evolve to meet these needs [50]. The potential of insect repellent as a resin co-product pathway requires additional research to fully explore its possibilities.

Guayule resin has been shown to be a sustainable alternative to traditional petroleum-based asphalt binders due to its ability to enhance the elasticity of asphalt and to reduce its susceptibility to cracking and aging [2]. Most of the asphalt binder research has been conducted on whole resin, rather than separated fractions. In this study, the blends of LMWR and the residuals from essential oil and insect repellent separations are expected to behave similarly to whole guayule resin when used as an asphalt binder. Further research is needed to confirm the extent to which the LMWR is the primary contributor to the asphalt binder properties of guayule resin and thus, enable value assessments of those fractions of separated resin.

Another promising area for future guayule bioeconomy research is the quantification of soil carbon in guayule cultivation. Guayule holds significant potential for carbon offsetting, however, the availability of direct physical measurements is very limited for the earliest part of the supply chain. To address this gap, research to quantitatively evaluate the greenhouse gas reduction and capture for the crop and the soil domains, through the combined utilization of direct field measurements and mathematical modeling, is needed. This will enable comparisons of the impacts of different crop management practices on soil emissions and the overall crop greenhouse gas budget, while reducing the potential for double counting.

The current evaluation of resin co-product pathways focuses on domestic or North American markets. However, there is potential for market expansion by assessing non-North American settings. Expanding markets beyond North America offers opportunities for increased profitability in all three resin co-product pathways, particularly the essential oil co-product pathway.

Within the aspen process models, natural gas significantly contributes to operating costs and emissions. To address this, heat integration and optimization can be implemented during the extraction process of guayule rubber, resin, and bagasse. These measures aim to reduce costs and emissions associated with heating requirements for heaters and distillation column reboilers.

Isomerization is a process that converts alpha-pinene to beta-pinene by rearranging the double bond. Various methods, including catalytic isomerization or chemical reactions, can be utilized. One advantage of isomerization is the elimination of the need for the third distillation column in the essential oil process model, resulting in cost reduction and decreased utility requirements. This further enhances the economic and environmental feasibility of a resin to essential oil co-product pathway.

CHAPTER 4: CONCLUSION

This study represents the first comprehensive examination of the economic and environmental implications of guayule resin co-product pathways: essential oils, insect repellent, and resin blend adhesive. The minimum selling price of guayule rubber is currently \$3.05 per kg, which places guayule rubber at the high end of the existing hevea rubber market. By selecting resin blend adhesive as a resin co-product, the minimum rubber selling price can be reduced to \$1.69 per kg, which enhances the overall economic viability of guayule. Using a combined economic and displacement allocation assessment method, the resin blend adhesive pathway also decreases the greenhouse gas emissions associated with rubber production by displacing traditional urea formaldehyde adhesive. This reduction can make the calculated emissions from guayule rubber more competitive with those of other natural and synthetic rubber sources. Further research on the repellency of guayule resin for additional insects may provide a more feasible bio-based repellent production pathway, while experimental work on fractionated resin for asphalt binder applications can enhance the understanding of guayule's overall economic viability and environmental impact.

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APPENDIX

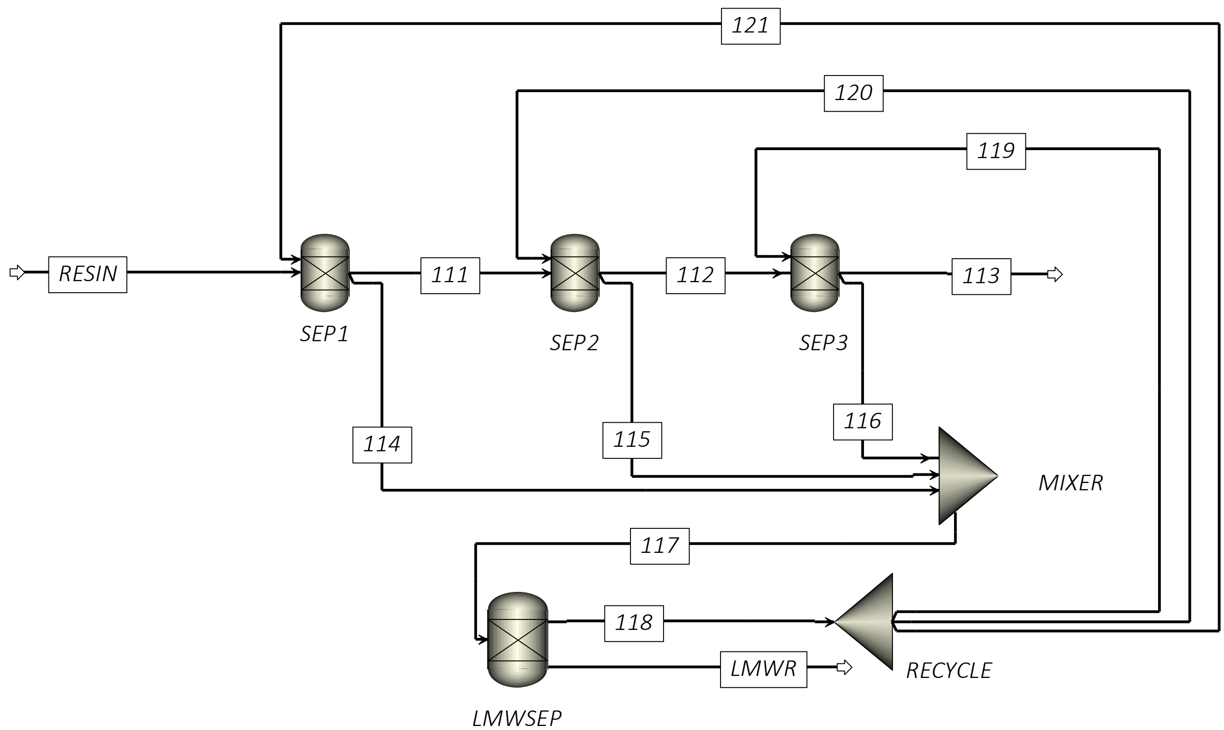

Figure A - 1: Process flow diagram of the removal of low-molecular weight rubber as modeled in Aspen Plus.

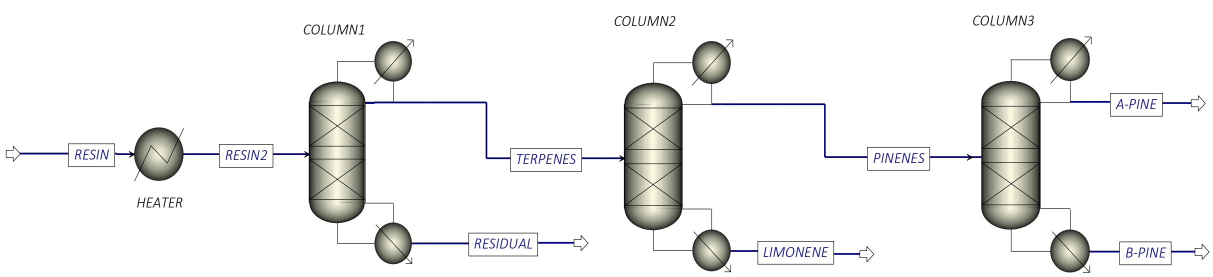

Figure A - 2: Process flow diagram of the separation of essential oils (monoterpenes) as modeled in Aspen Plus.

Table A - 1: Aspen Plus model parameters for the three vacuum distillation columns needed for production of essential oils.

Parameter	Column 1	Column 2	Column 3

Number of Stages	7	20	28
Distillate Rate (kmol/hr)	0.699	0.544	0.428
Reboiler Duty (J/sec)	19.2+05	5.19E+04	14.6E+04
Feed Stream (above-stage convention)	5	11	14
Pressure (Pa)	620	620	620
Start Stage	2	2	2
End Stage	6	19	27
Internal Type	packed	packed	packed
Packing Type	PALL	PALL	PALL
Packing Material	metal	metal	metal
Section Packed Height (mm)	37	31.5	55
Column Diameter (m)	3.98	1.06	1.28

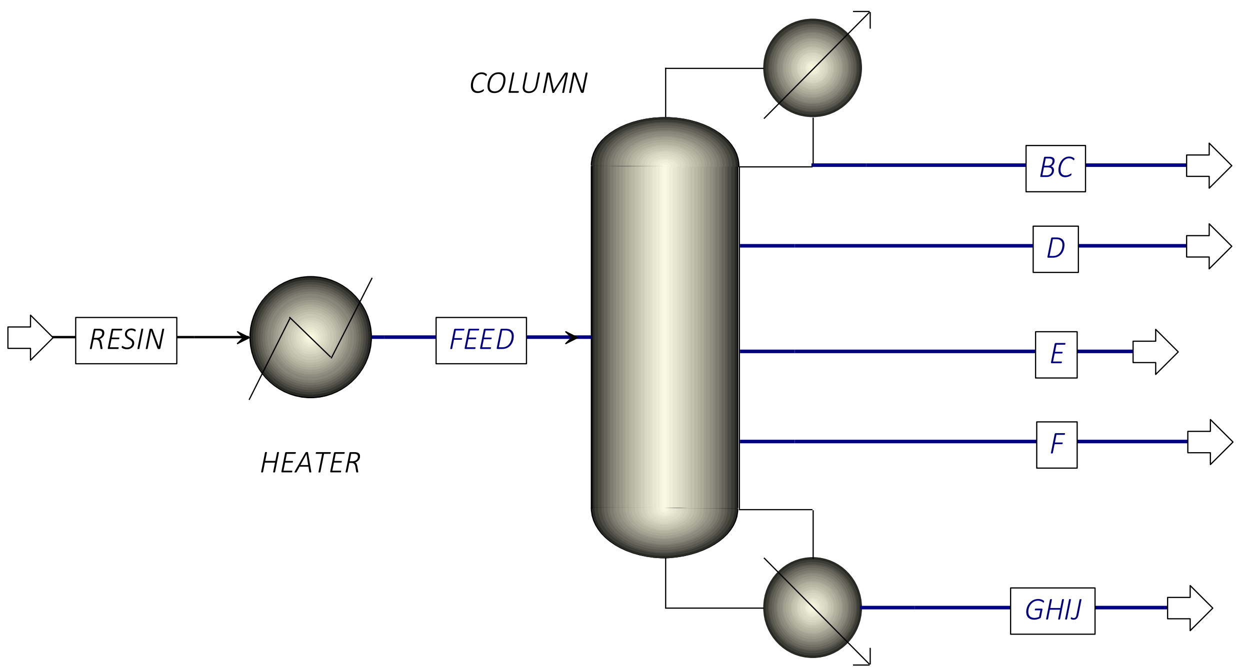

Figure A - 3: Process flow diagram for the production of the insect repellant as modeled in Aspen Plus.

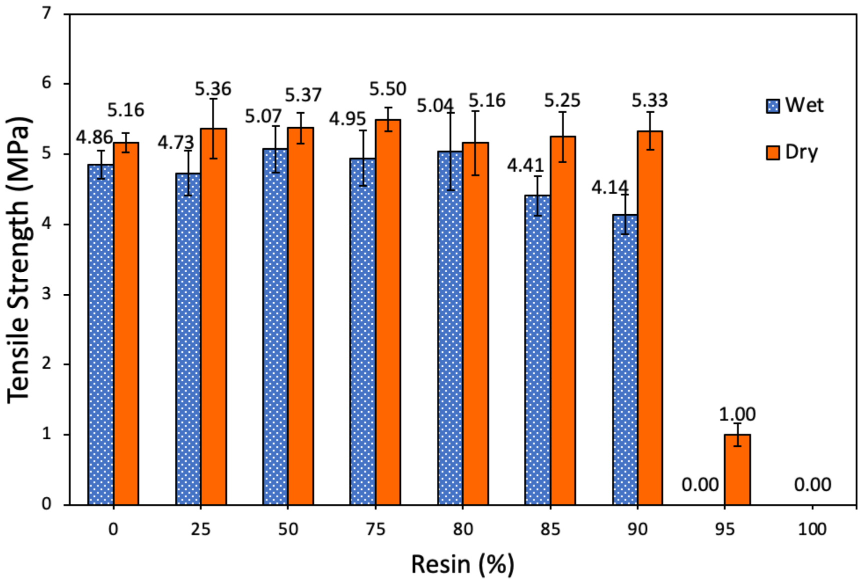

Figure A - 4: Adhesion test results of applying resin blend adhesive between two wood panels. Results show no significant difference of wet adhesion strength up to 85% blend and no significant difference of dry tensile strength of pure urea formaldehyde up to 90% replacement blend.

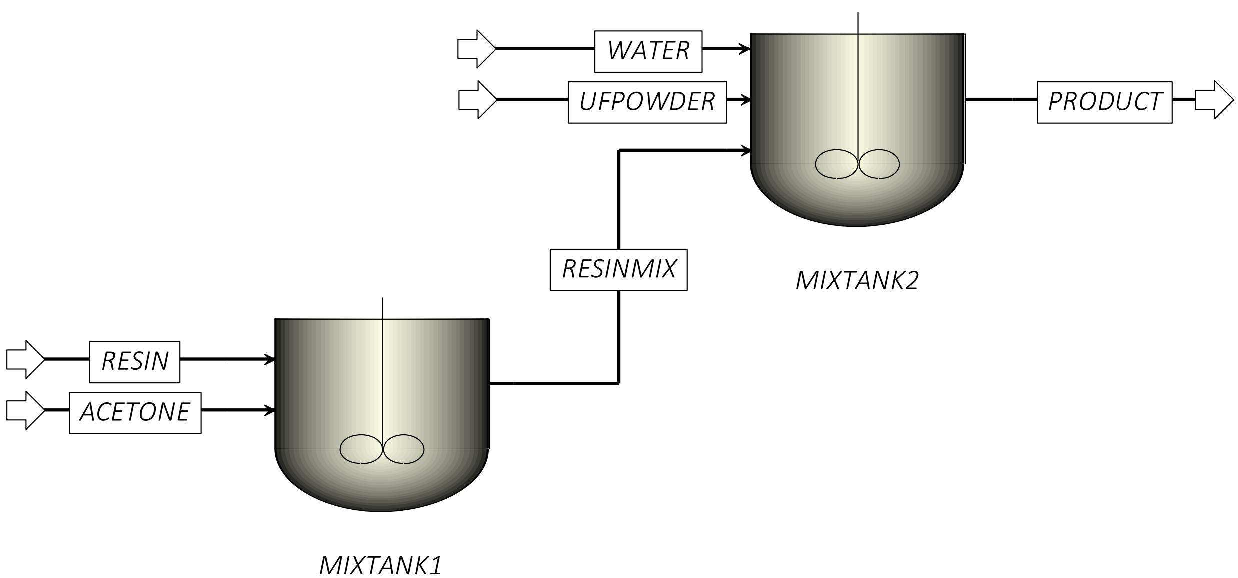

Figure A - 5: Process flow diagram for the production of the resin blend adhesive as modeled in Aspen Plus.

Table A - 2: Variable operating cost parameters for the evaluation of the guayule resin to products.

	Cost	Units
Industrial water	\$0.31	per tonne
Natural gas	\$0.01	per MJ
Electricity	\$0.059	per kWh
Sand	\$50	per tonne
Acetone	\$28	per kg
Urea Formaldehyde Powder	\$2.50	per kg

Table A - 3: Input parameters for techno-economic analysis used in the evaluation of the resin co-product pathways.

Parameter	Value
Project life	30 years
Project Year	2018
Operating Days per Year	350
Operating Hours	24/7
Internal rate of return	10%
Equity	40%
Loan interest	8%
Loan term	10 years
Working capital	5%
Construction period	3 years
Construction completed -- year 2	10%
Construction completed -- year 1	50%
Construction completed -- year 0	40%
Startup time	0.5 years
Production during start up	50%
Tax rate	35%
Depreciation	7 years MACRS[1]

[1] Modified accelerated cost recovery system.

Description	Units	118	121	120	119	117	114	115	116	LMWR	RESIN	111	112	113
From		LMWSEP	RECYCLE	RECYCLE	RECYCLE	MIXER	SEP1	SEP2	SEP3	LMWSEP		SEP1	SEP2	SEP3
To		RECYCLE	SEP1	SEP2	SEP3	LMWSEP	MIXER	MIXER	MIXER		SEP1	SEP2	SEP3	
Phase		Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase					Solid Phase				Liquid Phase
Temperature	C	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01	2.94E+01
Pressure	bar	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01	6.89E-01
Molar Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Molar Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.44E-01	6.80E-01	9.27E-01	9.97E-01	0.00E+00	4.15E-01	8.26E-01	9.94E-01	1.00E+00
Molar Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.56E-01	3.20E-01	7.30E-02	2.55E-03	1.00E+00	5.85E-01	1.74E-01	6.29E-03	0.00E+00
Mass Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mass Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.22E-01	6.44E-01	9.15E-01	9.97E-01	0.00E+00	7.50E-01	9.52E-01	9.99E-01	1.00E+00
Mass Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.78E-01	3.56E-01	8.46E-02	2.99E-03	1.00E+00	2.50E-01	4.76E-02	1.50E-03	0.00E+00
Molar Enthalpy	cal/mol	-5.89E+04	-5.89E+04	-5.89E+04	-5.89E+04	-4.97E+04	-4.00E+04	-5.46E+04	-5.87E+04	4.86E+01	-9.09E+06	-1.81E+07	-2.18E+07	-2.19E+07
Mass Enthalpy	cal/gm	-1.01E+03	-1.01E+03	-1.01E+03	-1.01E+03	-8.33E+02	-6.53E+02	-9.28E+02	-1.01E+03	7.13E-01	-5.71E+04	-7.25E+04	-7.60E+04	-7.61E+04
Molar Entropy	cal/mol-K	-7.39E+01	-7.39E+01	-7.39E+01	-7.39E+01	-6.23E+01	-5.02E+01	-6.85E+01	-7.37E+01	1.62E-01	-3.00E+04	-5.97E+04	-7.18E+04	-7.23E+04
Mass Entropy	cal/gm-K	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.05E+00	-8.19E-01	-1.16E+00	-1.27E+00	2.37E-03	-1.89E+02	-2.39E+02	-2.51E+02	-2.51E+02
Molar Density	mol/cc	1.35E-02	1.35E-02	1.35E-02	1.35E-02	1.50E-02	1.69E-02	1.41E-02	1.35E-02	3.70E-02	7.89E-03	4.44E-03	3.77E-03	3.75E-03
Mass Density	gm/cc	7.83E-01	7.83E-01	7.83E-01	7.83E-01	8.93E-01	1.04E+00	8.32E-01	7.85E-01	2.52E+00	1.26E+00	1.11E+00	1.08E+00	1.08E+00
Enthalpy Flow	cal/sec	-8.96E+05	-2.99E+05	-3.06E+05	-2.92E+05	-8.96E+05	-2.98E+05	-3.06E+05	-2.92E+05	1.36E+02	-4.37E+07	-4.37E+07	-4.37E+07	-4.37E+07
Average MW		5.81E+01	5.81E+01	5.81E+01	5.81E+01	5.96E+01	6.13E+01	5.88E+01	5.81E+01	6.81E+01	1.59E+02	2.49E+02	2.86E+02	2.88E+02
Mole Flows	kmol/hr	5.48E+01	1.83E+01	1.87E+01	1.78E+01	6.49E+01	2.69E+01	2.02E+01	1.79E+01	1.01E+01	1.73E+01	8.71E+00	7.24E+00	7.19E+00
Mass Flows	kg/hr	3.18E+03	1.06E+03	1.09E+03	1.04E+03	3.87E+03	1.65E+03	1.19E+03	1.04E+03	6.89E+02	2.76E+03	2.17E+03	2.07E+03	2.07E+03
Volume Flow	l/min	6.77E+01	2.26E+01	2.31E+01	2.20E+01	7.23E+01	2.64E+01	2.38E+01	2.21E+01	4.56E+00	3.66E+01	3.27E+01	3.20E+01	3.20E+01

Figure A - 6: Aspen Plus stream results summary for low-molecular weight rubber removal.

Table A - 4: Aspen Plus economics project capital cost summary for removal of low-molecular weight rubber from resin stream.

PROJECT CAPITAL SUMMARY		Total Cost	Design, Engineering, Procurement	Construction Material	Construction Manhours	Construction Manpower	Construction Indirects
Purchased Equipment	Cost	5.47E+04		5.47E+04			
Equipment Setting	Cost	2.53E+03			7.37E+01	2.53E+03	
Piping	Cost	9.91E+04		5.63E+04	1.28E+03	4.28E+04	
Civil	Cost	2.14E+04		1.11E+04	3.78E+02	1.02E+04	
Steel	Cost	2.56E+04		2.18E+04	1.19E+02	3.74E+03	
Instrumentation	Cost	3.15E+05		2.92E+05	6.80E+02	2.29E+04	
Electrical	Cost	3.76E+05		3.24E+05	1.62E+03	5.23E+04	
Insulation	Cost				0.00E+00		
Paint	Cost	1.28E+04		4.07E+03	3.55E+02	8.76E+03	
Other	Cost	9.08E+05	5.50E+05	7.84E+04			2.79E+05
G and A Overheads	Cost	3.79E+04		2.53E+04		4.30E+03	8.36E+03
Contract Fee	Cost	1.18E+05	4.46E+04	2.69E+04		1.58E+04	3.07E+04
Contingencies	Cost	3.55E+05	1.07E+05	1.61E+05		2.94E+04	5.72E+04
Total Project Cost	Cost	2.33E+06					

Description	Units	A-PINE	B-PINE	LIMONENE	PINENES	RESIDUAL	RESIN	RESIN 2	TERPENES
From		COLUMN3	COLUMN3	COLUMN2	COLUMN2	COLUMN1		HEATER	COLUMN1
To					COLUMN3		HEATER	COLUMN1	COLUMN2
Phase		Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase		Liquid Phase
Temperature	C	2.62E+01	3.28E+01	4.16E+01	2.72E+01	1.44E+02	2.94E+01	1.35E+02	2.84E+01
Pressure	bar	6.21E-03	6.21E-03	6.21E-03	6.21E-03	6.21E-03	6.89E-01	6.21E-03	6.21E-03
Molar Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.59E-01	0.00E+00
Molar Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.41E-01	1.00E+00
Molar Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mass Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.80E-02	0.00E+00
Mass Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.22E-01	1.00E+00
Mass Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Molar Enthalpy	cal/mol	-3.79E+03	-1.69E+03	-1.21E+04	-3.44E+03	-2.30E+07	-2.18E+07	-1.96E+07	-4.57E+03
Mass Enthalpy	cal/gm	-2.79E+01	-1.24E+01	-8.85E+01	-2.52E+01	-7.34E+04	-7.58E+04	-6.81E+04	-3.36E+01
Molar Entropy	cal/mol-K	-1.76E+02	-1.90E+02	-1.55E+02	-1.78E+02	-5.53E+04	-7.20E+04	-4.80E+04	-1.74E+02
Mass Entropy	cal/gm-K	-1.29E+00	-1.40E+00	-1.14E+00	-1.30E+00	-1.76E+02	-2.50E+02	-1.67E+02	-1.28E+00
Molar Density	mol/cc	6.29E-03	6.31E-03	6.07E-03	6.29E-03	3.30E-03	3.74E-03	1.15E-06	6.27E-03
Mass Density	gm/cc	8.57E-01	8.59E-01	8.27E-01	8.57E-01	1.04E+00	1.08E+00	3.31E-04	8.54E-01
Enthalpy Flow	cal/sec	-7.59E+02	-7.22E+01	-4.24E+02	-8.34E+02	-3.67E+07	-4.08E+07	-3.66E+07	-1.27E+03
Average MW		1.36E+02	1.36E+02	1.36E+02	1.36E+02	3.14E+02	2.88E+02	2.88E+02	1.36E+02
Mole Flows	kmol/hr	7.20E-01	1.53E-01	1.27E-01	8.73E-01	5.73E+00	6.73E+00	6.73E+00	1.00E+00
Mass Flows	kg/hr	9.81E+01	2.09E+01	1.72E+01	1.19E+02	1.80E+03	1.94E+03	1.94E+03	1.36E+02
Volume Flow	l/min	1.91E+00	4.05E-01	3.47E-01	2.31E+00	2.90E+01	3.00E+01	9.73E+04	2.66E+00

Figure A - 7: Aspen Plus stream results summary for essential oils co-product.

Table A - 5: Aspen Plus economics project capital cost summary for production of essential oils co-product.

PROJECT CAPITAL SUMMARY		Total Cost	Design, Engineering, Procurement	Construction Material	Construction Manhours	Construction Manpower	Construction Indirects
Purchased Equipment	Cost	3.70E+05		3.70E+05			
Equipment Setting	Cost	1.30E+04			3.88E+02	1.30E+04	
Piping	Cost	5.46E+05		3.53E+05	5.78E+03	1.93E+05	
Civil	Cost	8.86E+04		4.72E+04	1.53E+03	4.14E+04	
Steel	Cost	7.11E+04		6.06E+04	3.35E+02	1.05E+04	
Instrumentation	Cost	6.75E+05		5.58E+05	3.46E+03	1.18E+05	
Electrical	Cost	3.90E+05		3.33E+05	1.77E+03	5.71E+04	
Insulation	Cost	6.52E+04		3.54E+04	1.17E+03	2.97E+04	
Paint	Cost	4.65E+04		1.43E+04	1.30E+03	3.21E+04	
Other	Cost	2.37E+06	1.48E+06	1.82E+05			7.02E+05
G and A Overheads	Cost	9.45E+04		5.86E+04		1.48E+04	2.11E+04
Contract Fee	Cost	2.50E+05	9.49E+04	4.02E+04		4.74E+04	6.73E+04
Contingencies	Cost	8.96E+05	2.84E+05	3.69E+05		1.00E+05	1.42E+05
Total Project Cost	Cost	5.87E+06					

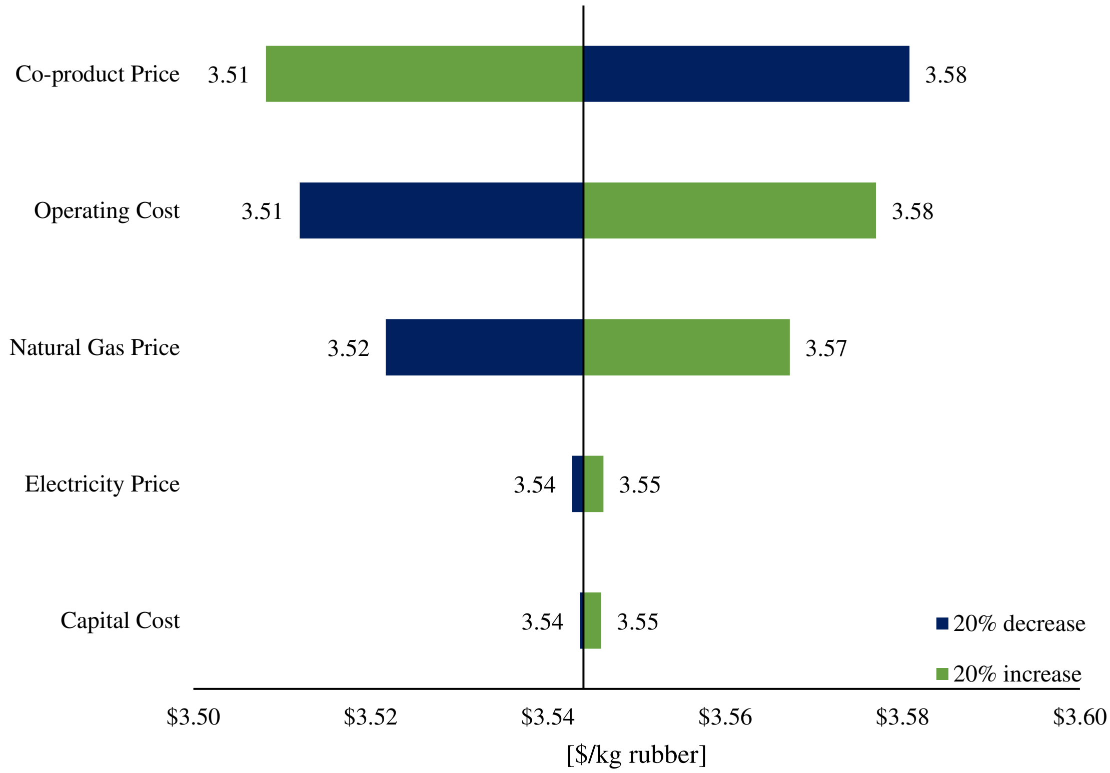

Figure A - 8: Results of sensitivity analysis of economic and flow parameters of essential oil process model and impact on minimum rubber selling price. Abbreviations: Internal rate of return: IRR.

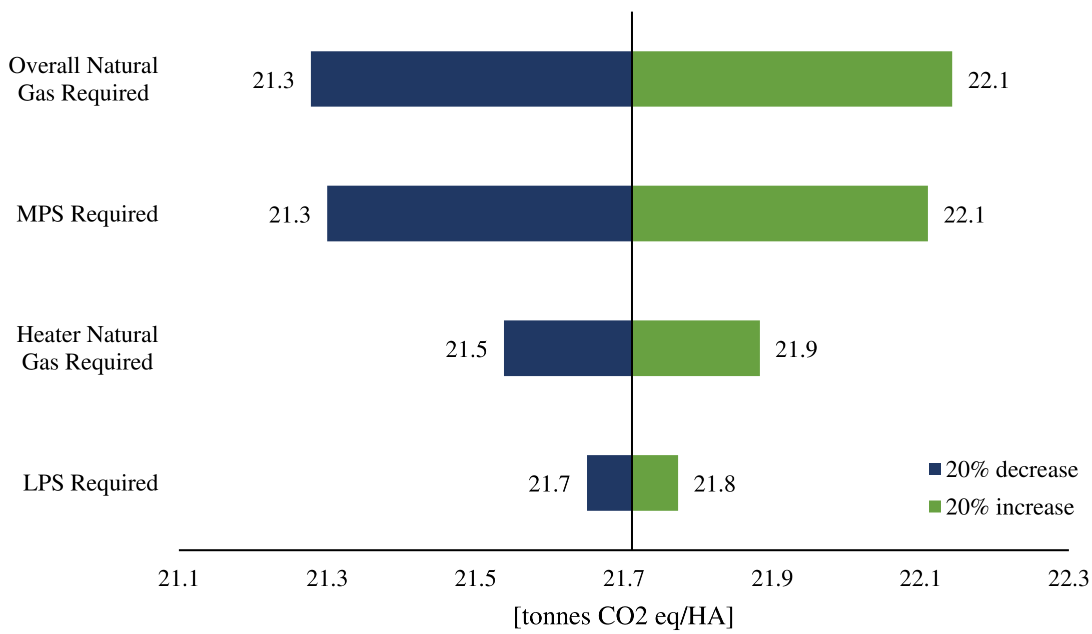

Figure A - 9: Results of sensitivity analysis of flow parameters of essential oil process model and impact on global warming potential. Abbreviations: Medium pressure steam: MPS, Low pressure steam: LPS.

Description	Units	BC	D	E	F	FEED	GHIG	RESIN
From		COLUMN	COLUMN	COLUMN	COLUMN	HEATER	COLUMN	
To						COLUMN		VACDIST
Phase		Liquid Phase	Liquid Phase	Liquid Phase	Liquid Phase		Liquid Phase	Liquid Phase
Temperature	C	2.00E+01	1.00E+02	2.00E+02	2.02E+02	1.60E+02	2.15E+02	2.94E+01
Pressure	bar	1.38E-02	1.38E-02	1.38E-02	1.38E-02	1.38E-02	1.38E-02	6.89E-02
Molar Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.68E-01	0.00E+00	0.00E+00
Molar Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	8.32E-01	1.00E+00	1.00E+00
Molar Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mass Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	8.50E-02	0.00E+00	0.00E+00
Mass Liquid Fraction		1.00E+00	1.00E+00	1.00E+00	1.00E+00	9.15E-01	1.00E+00	1.00E+00
Mass Solid Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Molar Enthalpy	cal/mol	-1.38E+05	-2.72E+07	-2.25E+07	-2.28E+07	-1.89E+07	-1.87E+07	-2.18E+07
Mass Enthalpy	cal/gm	-1.01E+03	-1.23E+05	-7.10E+04	-7.15E+04	-6.58E+04	-5.46E+04	-7.58E+04
Molar Entropy	cal/mol-K	-6.31E+02	-7.29E+04	-4.75E+04	-4.80E+04	-4.37E+04	-3.84E+04	-7.20E+04
Mass Entropy	cal/gm-K	-4.60E+00	-3.28E+02	-1.50E+02	-1.51E+02	-1.52E+02	-1.12E+02	-2.50E+02
Molar Density	mol/cc	6.30E-03	4.43E-03	3.13E-03	3.10E-03	2.29E-06	2.94E-03	3.74E-03
Mass Density	gm/cc	8.64E-01	9.85E-01	9.90E-01	9.89E-01	6.58E-04	1.01E+00	1.08E+00
Enthalpy Flow	cal/sec	-4.00E+04	-3.78E+06	-1.07E+07	-1.37E+07	-3.54E+07	-6.80E+06	-4.08E+07
Average MW		1.37E+02	2.22E+02	3.16E+02	3.19E+02	2.88E+02	3.42E+02	2.88E+02
Mole Flows	kmol/hr	1.04E+00	5.00E-01	1.71E+00	2.17E+00	6.73E+00	1.31E+00	6.73E+00
Mass Flows	kg/hr	1.43E+02	1.11E+02	5.40E+02	6.92E+02	1.94E+03	4.49E+02	1.94E+03
Volume Flow	l/min	2.76E+00	1.88E+00	9.10E+00	1.17E+01	4.90E+04	7.42E+00	3.00E+01

Figure A - 10: Aspen Plus stream results summary for insect repellant co-product.

Table A - 6: Aspen Plus economics project capital cost summary for production of insect repellant co-product.

PROJECT CAPITAL SUMMARY- insect repellant		Total Cost	Design, Engineering, Procurement	Construction Material	Construction Manhours	Construction Manpower	Construction Indirects
Purchased Equipment	Cost	1.71E+05		1.71E+05			
Equipment Setting	Cost	8.29E+03			2.50E+02	8.29E+03	
Piping	Cost	2.09E+05		1.16E+05	2.79E+03	9.31E+04	
Civil	Cost	4.34E+04		2.27E+04	7.61E+02	2.07E+04	
Steel	Cost	3.04E+04		2.57E+04	1.48E+02	4.64E+03	
Instrumentation	Cost	4.74E+05		4.14E+05	1.78E+03	6.03E+04	
Electrical	Cost	5.09E+05		4.38E+05	2.19E+03	7.08E+04	
Insulation	Cost	5.39E+04		2.94E+04	9.68E+02	2.45E+04	
Paint	Cost	1.57E+04		4.54E+03	4.50E+02	1.12E+04	
Other	Cost	1.56E+06	9.53E+05	1.25E+05			4.78E+05
Subcontracts	Cost	0.00E+00					
G and A Overheads	Cost	6.35E+04	0.00E+00	4.04E+04		8.80E+03	1.43E+04
Contract Fee	Cost	1.95E+05	7.34E+04	4.02E+04		3.11E+04	5.07E+04
Escalation	Cost	0.00E+00	0.00E+00	0.00E+00		0.00E+00	0.00E+00
Contingencies	Cost	5.99E+05	1.85E+05	2.57E+05		6.00E+04	9.77E+04
Special Charges	Cost	0.00E+00					

Total Project Cost	Cost	2.90E+06					

Table A - 7: Breakdown of ingredient composition and pricing data for 9 bio-based cockroach repellants commercially available.

Active Ingredient Pricing Data				
Cockroach Repellant Active Ingredient Composition and Fraction				
Wondercide® Natural Indoor Pest Control	cedarwood oil	%	4.2	Wondercide®
Spray	peppermint oil	%	1.5	
Wondercide® Natural Ant & Roach	geranium oil	%	1.47	Wondercide®
	lemongrass oil	%	0.10	
Eco Defense Biobased Pest Control	geranium oil	%	0.11	Ecodefense
Spray	peppermint oil	%	1.0	
Bug Botanist® Ant & Roach Remedy	geranium oil	%	6.2	Bug Botanist®
	lemongrass oil	%	0.5	
MDXconcepts© Organic Home Pest	peppermint oil	%	2.0	Mdxconcepts
Control Spray	rosemary oil	%	1.0	
	spearmint oil	%	1.0	
Ortho® Home Defense® Ant & Roach	cinnamon oil	%	0.36	Ortho®
Killer with Essential Oils	geranium oil	%	0.21	
	castor oil	%	0.14	
	cornmint oil	%	0.07	
	clove oil	%	0.07	
ZapNatural Pest Control Spray	Clove oil	%	0.05	Amazon®
	cottonseed oil	%	0.05	
Ecosmart Ant & Roach Killer	peppermint oil	%	1.5	Ecosmart
	rosemary oil	%	1.5	
Mighty Mint® Roach Repellant	peppermint oil	%	4.0	Mighty Mint®
Active Ingredient Market Price				
Cedarwood oil		$/kg	23.40	(Başer, 2016)
Peppermint oil		$/kg	15.69	(Intracen, 2019)
Geranium oil		$/kg	80.85	(Narnoliya, 2019)
Lemongrass oil		$/kg	41.18	(Intracen, 2019)
Rosemary oil		$/kg	44.12	(Intracen, 2019)
Spearmint oil		$/kg	38.44	(Başer, 2016)
Cinnamon oil		$/kg	75.49	(Intracen, 2019)
Castor oil		$/kg	1.96	(Dumeignil, 2012)
Cornmint oil		$/kg	17.55	(Başer, 2016)
Clove oil		$/kg	20.06	(Başer, 2016)
Cottonseed oil		$/kg	0.74	(USDA, 2021)
Mass Average Active Ingredient Baseline Price		$/kg	41.40	

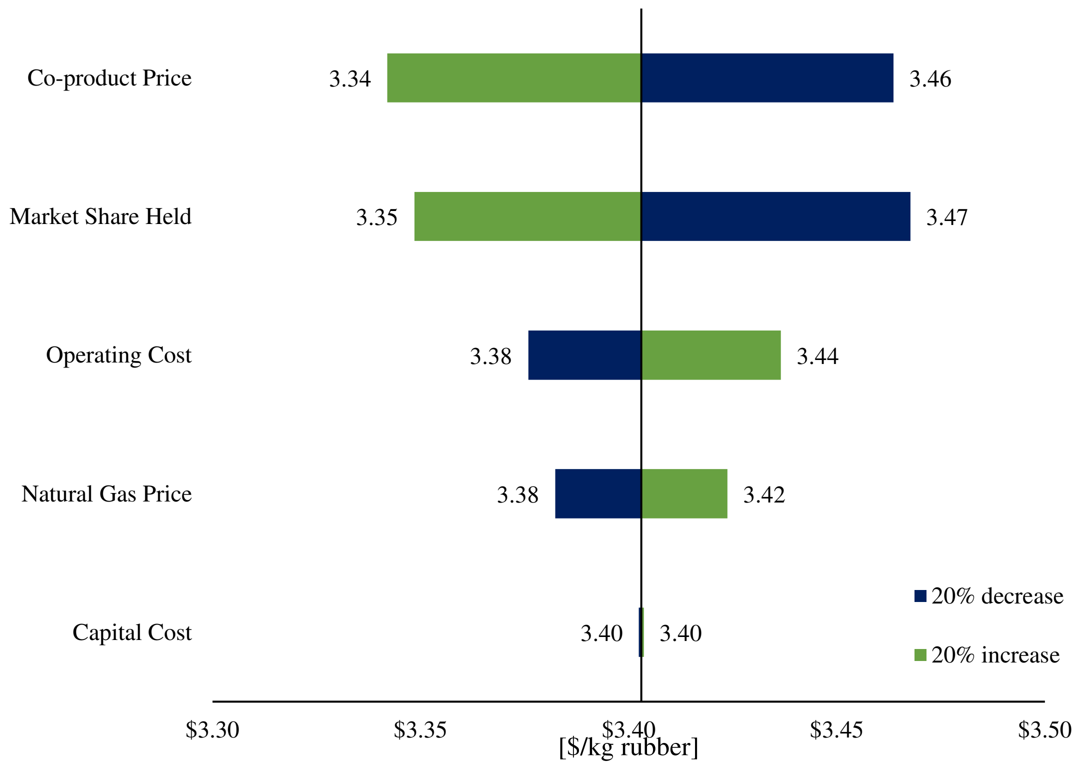

Figure A - 11: Results of sensitivity analysis of economic and flow parameters of insect repellant process model and impact on minimum rubber selling price. Abbreviations: Internal rate of return: IRR.

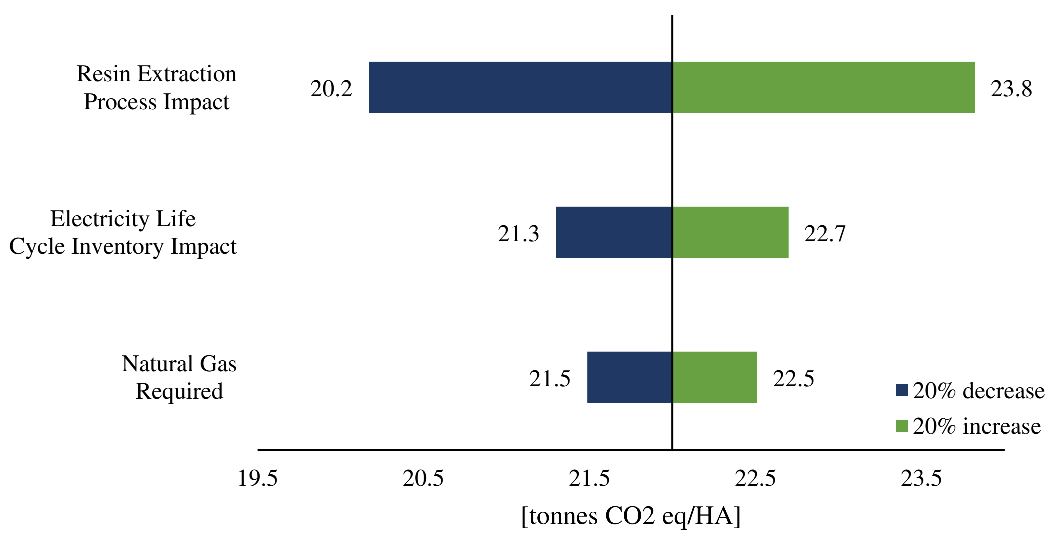

Figure A - 12: Results of sensitivity analysis of flow parameters of insect repellant process model and impact on global warming potential.

Description	Units	ACETONE	PRODUCT	RESIN	RESINMIX	UFPOWDER	WATER
From			MIXTANK2		MIXTANK1		
To		MIXTANK1		MIXTANK1	MIXTANK2	MIXTANK2	MIXTANK2
Phase		Liquid Phase		Liquid Phase	Liquid Phase		Liquid Phase
Temperature	C	2.94E+01	1.50E+02	2.94E+01	1.50E+02	2.94E+01	2.90E+01
Pressure	bar	6.89E-01	2.00E+01	6.89E-01	2.00E+01	6.89E-01	1.00E+00
Molar Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.00E-01	0.00E+00
Molar Liquid Fraction		1.00E+00	9.32E-01	1.00E+00	1.00E+00	0.00E+00	1.00E+00
Molar Solid Fraction		0.00E+00	6.85E-02	0.00E+00	0.00E+00	5.00E-01	0.00E+00
Mass Vapor Fraction		0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.33E-01	0.00E+00
Mass Liquid Fraction		1.00E+00	9.44E-01	1.00E+00	1.00E+00	0.00E+00	1.00E+00
Mass Solid Fraction		0.00E+00	5.60E-02	0.00E+00	0.00E+00	6.67E-01	0.00E+00
Molar Enthalpy	cal/mol	-5.89E+04	-2.42E+06	-2.18E+07	-4.04E+06	-5.27E+04	-6.82E+04
Mass Enthalpy	cal/gm	-1.01E+03	-3.30E+04	-7.58E+04	-3.84E+04	-1.17E+03	-3.79E+03
Molar Entropy	cal/mol-K	-7.38E+01	-5.66E+03	-7.20E+04	-9.50E+03	-5.62E+01	-3.87E+01
Mass Entropy	cal/gm-K	-1.27E+00	-7.71E+01	-2.50E+02	-9.04E+01	-1.25E+00	-2.15E+00
Molar Density	mol/cc	1.35E-02	1.06E-02	3.74E-03	7.33E-03	5.47E-05	5.50E-02
Mass Density	gm/cc	7.83E-01	7.79E-01	1.08E+00	7.70E-01	2.47E-03	9.90E-01
Enthalpy Flow	cal/sec	-4.28E+05	-3.73E+07	-4.08E+07	-3.69E+07	-1.11E+05	-2.82E+05
Average MW		5.81E+01	7.34E+01	2.88E+02	1.05E+02	4.50E+01	1.80E+01
Mole Flows	kmol/hr	2.62E+01	5.54E+01	6.73E+00	3.29E+01	7.58E+00	1.49E+01
Mass Flows	kg/hr	1.52E+03	4.06E+03	1.94E+03	3.45E+03	3.41E+02	2.68E+02
Volume Flow	l/min	3.23E+01	8.69E+01	3.00E+01	7.48E+01	2.31E+03	4.52E+00

Figure A - 13: Aspen Plus stream results summary for resin blend adhesive co-product.

Table A - 8: Aspen Plus economics project capital cost summary for production of resin blend adhesive co-product.

PROJECT CAPITAL SUMMARY		Total Cost	Design, Engineering, Procurement	Construction Material	Construction Manhours	Construction Manpower	Construction Indirects
Purchased Equipment	Cost	2.69E+05		2.69E+05		2.69E+05	
Equipment Setting	Cost	2.11E+03		2.11E+03		0.00E+00	6.12E+01
Piping	Cost	6.25E+04		6.25E+04		3.00E+04	9.78E+02
Civil	Cost	1.87E+04		1.87E+04		9.85E+03	3.26E+02
Steel	Cost	1.66E+04		1.66E+04		1.42E+04	7.74E+01
Instrumentation	Cost	3.69E+05		3.69E+05		3.26E+05	1.25E+03
Electrical	Cost	3.92E+05		3.92E+05		3.36E+05	1.74E+03
Insulation	Cost	2.93E+04		2.93E+04		1.47E+04	5.80E+02
Paint	Cost	4.34E+03		4.34E+03		1.20E+03	1.25E+02
Other	Cost	8.90E+05	5.05E+05	8.90E+05	5.05E+05	1.03E+05	
G and A Overheads	Cost	4.65E+04		4.65E+04		3.31E+04	
Contract Fee	Cost	1.21E+05	4.19E+04	1.21E+05	4.19E+04	3.07E+04	
Contingencies	Cost	4.00E+05	9.85E+04	4.00E+05	9.85E+04	2.10E+05	
Total Project Cost	Cost	2.62E+06		2.62E+06			

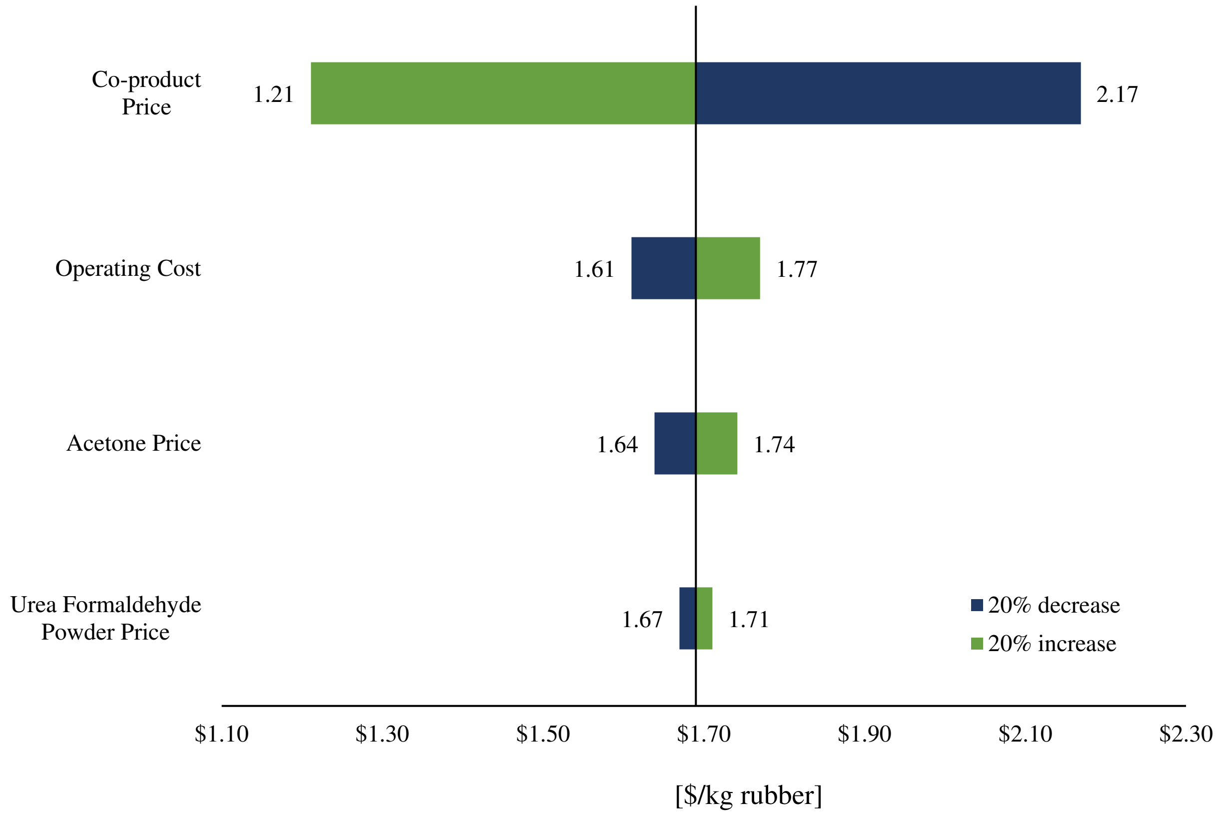

Figure A - 14: Results of sensitivity analysis of economic and flow parameters of resin blend adhesive process model and impact on minimum rubber selling price. Abbreviations: Internal rate of return: IRR.

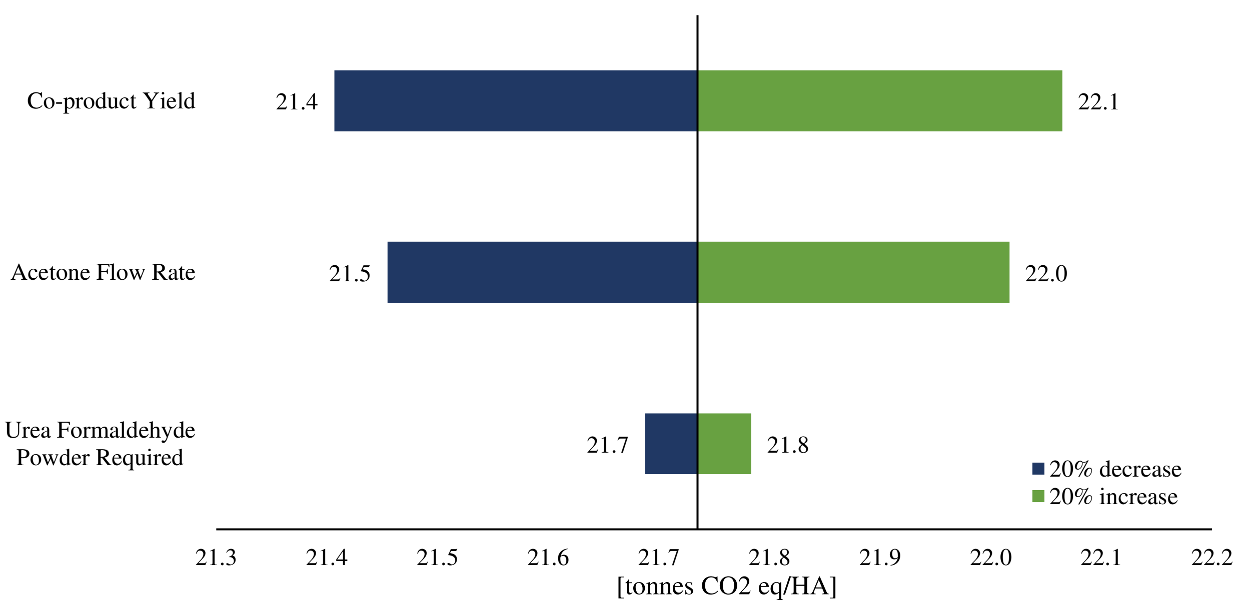

Figure A - 15: Results of sensitivity analysis of flow parameters of resin blend adhesive process model and impact on global warming potential.