

# Bi-Weekly Report 2:

## Process Development for Solketal Production from Glycerol

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## Property analysis and identification of operating conditions

The data compiled in this section forms the quantitative basis for the selection of operating conditions, the choice of thermodynamic models, the specification of equipment, and the development of safety protocols.

### 1.1 Physicochemical Properties of Process Components

The process involves four primary chemical components: the reactants, glycerol and acetone; and the products, solketal and water. A summary of their key physicochemical properties is presented in Table 2.1.

- An important feature of this chemical system is the **wide distribution of boiling points** among its components. Acetone, with a boiling point of 56.05°C, is exceptionally volatile compared to water (100°C), solketal (~188°C), and especially glycerol (290°C).
- The pronounced volatility of acetone dictates that it should be the first component removed from the reactor effluent. This **direct sequence** approach—removing the most volatile component first, minimizes the thermal duty on subsequent separation units, this fundamental property directly leads to the design of the first major separation unit as an Acetone Recovery Column, which also facilitates the efficient recycling of the unreacted excess acetone.

- Furthermore, crude glycerol is a syrupy, highly viscous liquid, with a viscosity of approximately 1499 cP at 20°C. In stark contrast, acetone is a very low-viscosity fluid (~0.3 cP at 25°C), and the product solketal has a moderately low viscosity (~11 cP at 25°C). To ensure reliable and efficient transport of the viscous glycerol from storage to the reactor, **positive displacement pumps, such as gear or progressive cavity pumps, are required** instead of standard centrifugal pumps, which perform poorly with high-viscosity fluids.
- To overcome potential mass transfer limitations and ensure a homogeneous feed to the reactor, the feed mixing tank must be equipped with a **high-torque agitator** capable of effectively blending these two disparate phases.

**Table 2.1: Comparative Physicochemical Properties of Process Components**

Property	Glycerol	Acetone	Solketal	Water
<b>Molecular Formula</b>	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> O	C <sub>6</sub> H <sub>12</sub> O <sub>3</sub>	H <sub>2</sub> O
<b>Molecular Weight (g/mol)</b>	92.09	58.08	132.16	18.02
<b>Boiling Point (°C at 1 atm)</b>	290 (decomposes)	56.05	188 - 189	100
<b>Melting/Freezing Point (°C)</b>	18.2	-94.7	~ -26	0
<b>Density (g/mL at 25°C)</b>	1.262	0.785	1.063	0.997
<b>Viscosity (cP at 25°C)</b>	~1412	0.295	11	0.89
<b>Flash Point (°C)</b>	160 - 199	-20	80 - 90	N/A
<b>Water Solubility</b>	Miscible	Miscible	Miscible	N/A

## 1.2 Thermodynamic Framework and Phase Behavior

Glycerol and water are highly polar protic molecules characterized by extensive intermolecular hydrogen bonding, which is responsible for their high boiling points and viscosity. Acetone is a

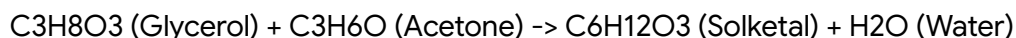
polar aprotic molecule. This mixture of different molecular functionalities leads to significant positive deviations from ideal solution behavior.

A critical aspect of this system is the limited miscibility between the primary reactants, glycerol and acetone. At the start of the process, the mixture can form two liquid phases, which would severely limit the reaction rate due to interfacial mass transfer resistance. However, as the reaction proceeds, the products—solketal and water—are formed. Solketal is completely miscible in water and most organic compounds, including the reactants. It effectively **acts as a co-solvent**, increasing the mutual solubility of glycerol and acetone and eventually leading to a single, homogeneous liquid phase in the reactor.

To accurately model this complex phase behavior, a sophisticated thermodynamic property package is required. As established in the first bi-weekly report, the Non-Random Two-Liquid (NRTL) activity coefficient model is the most appropriate choice for this system.

### 1.3 Process Chemistry and Stoichiometry

The synthesis of solketal is achieved through the acid-catalyzed ketalization of glycerol with acetone. The overall stoichiometric reaction is as follows:



This is a reversible condensation reaction that is limited by chemical equilibrium. To achieve high conversion of the valuable glycerol feedstock, the equilibrium must be shifted towards the products. This is typically accomplished by using a large molar excess of one reactant (acetone) or by continuously removing one of the products (water). This design will employ an excess of acetone.

**Formation of by-product:** The reaction is highly selective towards the desired product, solketal, which is a five-membered cyclic ketal. A six-membered ring isomer, (2,2-dimethyl-1,3-dioxan-5-ol), can also be formed, but it is a minor by-product, typically accounting for only about 2% of the product mixture. Given this high selectivity, the formation of the isomer can be reasonably neglected for the purposes of preliminary process design and simulation, simplifying the material balance calculations.

The ketalization reaction is exothermic, with a standard enthalpy of reaction ( $\Delta H_{rxn}$ ) reported to be approximately -20.1 kJ/mol. This is a relatively mild exotherm. The combination of this modest heat release with the selected low operating temperature (as discussed below) has a significant positive impact on the reactor design. The heat generated by the reaction can be effectively and safely removed using standard plant utility cooling water circulated through a jacket on the Continuous Stirred-Tank Reactor (CSTR).

### 1.4 Identification of Optimal Operating Conditions

The selected parameters represent a balance between maximizing reaction kinetics, achieving high conversion, and ensuring safe and stable process operability.

- **Temperature:** An operating temperature of **60°C** is selected. Multiple studies indicate that the optimal temperature range for this reaction using solid acid catalysts is between 40°C and 60°C. Selecting 60°C maximizes the reaction rate constant according to the Arrhenius equation, thereby minimizing the required reactor volume for a given production rate. While higher temperatures could further increase the rate, they also approach the atmospheric boiling point of acetone.
- **Pressure:** The reactor will be operated at a slightly elevated pressure of **2 to 3 atm**. The selected operating temperature of 60°C is above the normal boiling point of acetone (56.05°C). If the reactor were operated at atmospheric pressure, the acetone would boil, resulting in a two-phase vapor-liquid system. This would reduce the liquid-phase concentration of acetone, thereby lowering the reaction rate, and would also create a more complex system to control and model. We hence ensure that the reaction proceeds entirely within a single, predictable liquid phase.
- **Reactant Molar Ratio (Acetone:Glycerol):** A molar ratio of **6:1** is selected for the reactor feed. As an equilibrium-limited reaction, Le Châtelier's principle dictates that a high concentration of one reactant will drive the reaction forward. Literature confirms that using a molar excess of acetone in the range of 3:1 to 9:1 is effective for achieving high glycerol conversion. A ratio of 6:1 provides a strong driving force for the reaction while representing a balance: a much higher ratio would lead to an excessively large and costly acetone recovery and recycle loop.
- **Catalyst:** A solid acid catalyst, specifically a macroreticular sulfonic acid ion-exchange resin such as **Amberlyst-15** or **Amberlyst-46**, will be employed. The catalyst can be retained within the reactor (e.g., in a fixed bed or basket) or easily separated from the liquid effluent by simple filtration, making the process cleaner, more environmentally friendly, and more economical by reducing raw material consumption, waste treatment costs, and the number of required unit operations.
- **Target Conversion:** A per-pass glycerol conversion of **85%** is targeted in the CSTR. This is a realistic and achievable conversion level based on published experimental data for similar operating conditions. The finalized design parameters for the reaction section are summarized in Table 3.1.

**Table 1.4: Finalized Reactor Operating Conditions and Justification**

Parameter	Design Value	Justification / Rationale
Temperature	60°C	Maximizes reaction rate within the optimal range identified in literature, balancing kinetics against potential acetone vaporization.
Pressure	2 - 3 atm	Maintains the reaction mixture in a single liquid phase by elevating the boiling point of acetone above the operating temperature, ensuring stable and efficient operation.
Acetone:Glycerol Molar Ratio	6:1	Provides a significant excess of acetone to shift the reaction equilibrium towards high product yield, consistent with established practice.
Catalyst Type	Solid Acid Ion-Exchange Resin (e.g., Amberlyst-15)	Simplifies the process by eliminating the need for downstream neutralization and waste salt separation, reducing costs and environmental impact.
Target Per-Pass Glycerol Conversion	85%	Represents a realistic and achievable conversion in a single pass, with overall high conversion achieved via recycling of unreacted glycerol.

# Process synthesis and development of a process flow diagram

## 2.1 Unit Operation Sequencing

**Feed Section:** The process begins with the storage of raw materials. Crude glycerol (assumed 90 wt% purity) is stored in a dedicated tank (TK-101), and industrial-grade acetone (99 wt% purity) is stored in another (TK-102). From storage, the reactants are transferred via pumps (P-101 A/B, P-102 A/B) to a continuously stirred mixing tank (MX-101). This vessel is crucial for blending the fresh feeds with the large recycled acetone stream from the purification section. The high-torque agitator in MX-101 ensures the viscous glycerol is adequately dispersed into the acetone phase before entering the reactor.

**Reaction Section:** The combined, homogenized liquid feed from MX-101 is pumped (P-103 A/B) through a shell-and-tube heat exchanger (E-101), where it is pre-heated to the target reaction temperature of 60°C using low-pressure steam (LPS). The heated feed then enters the CSTR (R-101), where the ketalization reaction occurs in the presence of the solid acid catalyst. The reactor is equipped with a cooling jacket through which utility cooling water (CW) flows to remove the exothermic heat of reaction and maintain a constant temperature. The reactor effluent, now containing solketal, water, unreacted glycerol, and excess acetone, flows to a cooler (E-102) where its temperature is reduced using cooling water to prevent flashing before it enters the first distillation column.

**Separation Train:** The purification of the reactor effluent is achieved via a three-column distillation sequence. This design is the most robust and energy-efficient configuration for this four-component mixture. A system with N components generally requires N-1 separation steps for complete purification. For this four-component system, a three-column train is therefore necessary. The sequence follows the "direct sequence" heuristic, where components are removed one by one in order of decreasing volatility. This is the most logical approach given the vast differences in boiling points (Acetone << Water < Solketal << Glycerol).

1. **Acetone Recovery Column (T-101):** The cooled reactor effluent is fed to the first column. Due to its extremely high volatility relative to the other components, acetone is easily separated as the overhead distillate product. This stream, containing over 99% acetone, is condensed and recycled back to the feed mixing tank (MX-101). This constitutes the primary recycle loop required by the project constraints and is essential for the process economics, as it minimizes the consumption of fresh acetone. The bottoms product from T-101 is an acetone-free mixture of water, solketal, and unreacted glycerol.
2. **Dehydration Column (T-102):** The bottoms from T-101 are fed to the second distillation column. In this unit, water, being the next most volatile component, is separated as the

overhead distillate product. This stream can be sent to wastewater treatment. The bottoms product is now a binary mixture of the high-boiling components: solketal and unreacted glycerol.

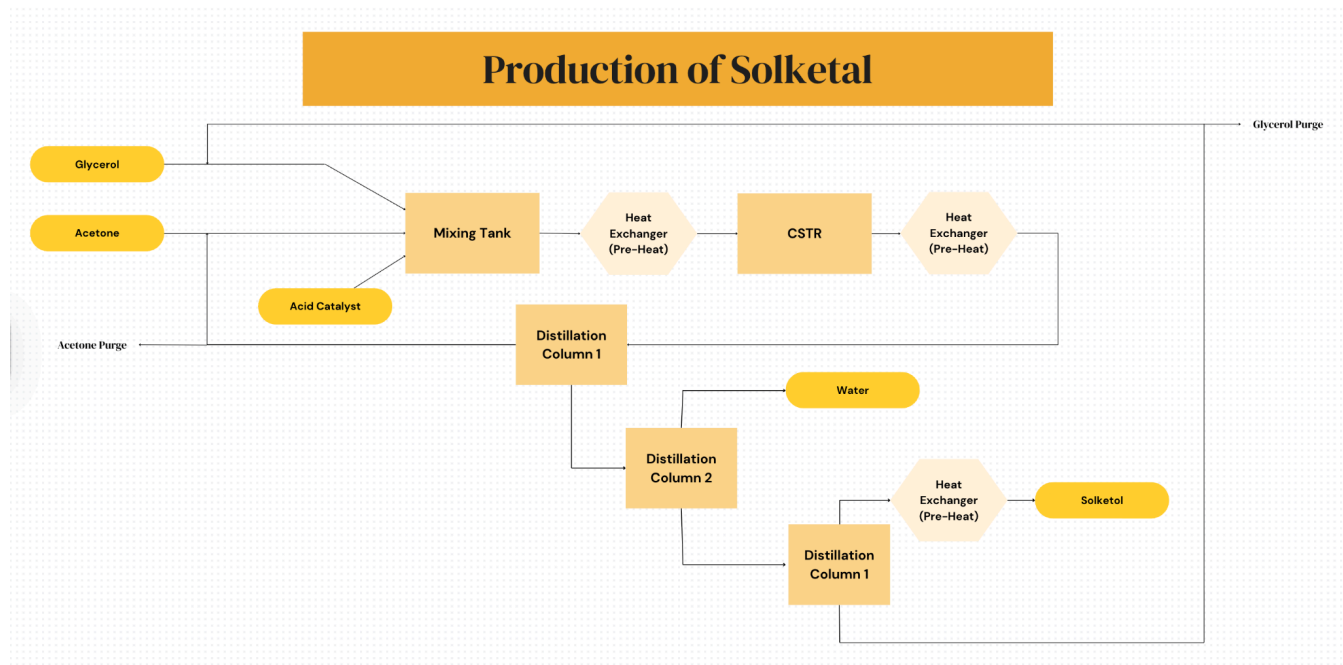
3. **Solketal Purification Column (T-103):** The bottoms from T-102 are fed to the final column, which performs the split between the product and the unreacted heavy reactant. Solketal (BP ~188°C) is the more volatile of the two and is taken as the high-purity (target >97%) overhead distillate product. After passing through a final product cooler (E-103), it is sent to product storage. The heavy bottoms product from this column is primarily unreacted glycerol (BP 290°C), which is recycled back and combined with the fresh glycerol feed upstream of the mixing tank. This second recycle loop maximizes the overall yield of the process.

This three-column sequence is energetically efficient because the largest stream component (the excess acetone) is removed first at the lowest temperature, avoiding the need to boil the entire reactor effluent to the much higher temperatures required to separate solketal and glycerol. This design satisfies the project requirement for at least two separation steps, including at least one distillation column.

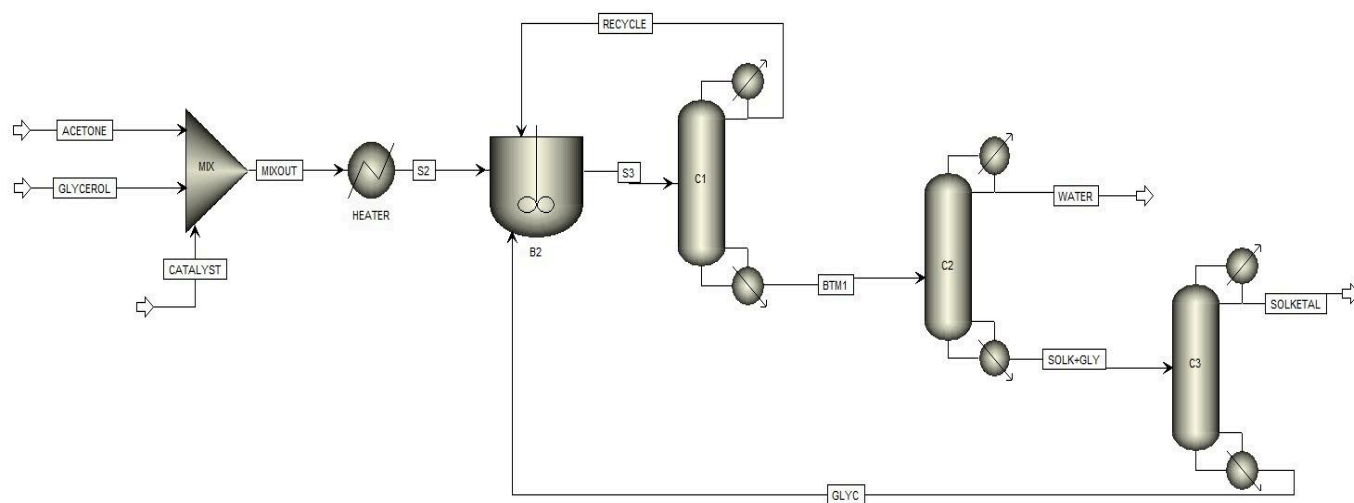
**Utility Integration:** As required by the project constraints, the process is designed to be integrated with site-wide utilities. The PFD shows connections to a cooling water loop (supplying CW to R-101, E-102, E-103, and all column condensers) which would be served by a cooling tower. It also shows connections to a steam system (supplying HPS or LPS to E-101 and all column reboilers) which would be generated by a captive Rankine cycle-based power plant. The process includes three heat exchangers (E-101, E-102, E-103) that are separate from the distillation column condensers and reboilers, satisfying another project constraint.

## 2.2 Detailed Process Flow Diagram (PFD)

The Process Flow Diagram (PFD) on the following page provides a detailed visual representation of the solketal production process, incorporating the design rationale described above. The diagram includes all major equipment units with unique identification tags, all primary process streams with numbered flags, key operating conditions, basic process control loops, and connections to major utility systems.



## Flowsheet development in Aspen Plus



The process for producing solketal from glycerol and acetone was modeled and simulated using Aspen Plus, a leading process simulation software. The flowsheet, as depicted in the provided diagram, was constructed to accurately represent the proposed unit operations and material streams.

The simulation began by defining the four key components—glycerol, acetone, solketal, and water—along with a solid acid catalyst. The **Non-Random Two-Liquid (NRTL)** activity



coefficient model was selected as the thermodynamic property package. This choice was critical because it accurately accounts for the significant non-ideal behavior of the mixture, particularly the limited miscibility between glycerol and acetone, and the strong hydrogen bonding present in the system.

The flowsheet was built sequentially, starting with the feed section. The fresh feeds of glycerol and acetone were introduced as separate streams and combined with the recycled streams in the **MIX** unit. This mixed stream, representing the feed to the reactor, was then heated to the target reaction temperature of 60°C in a **Heater** unit (representing the heat exchanger E-101 in the report). The core of the process, the exothermic ketalization reaction, was modeled within the **CSTR** unit (representing R-101). The reactor was specified to operate at a pressure of 2-3 atm and a temperature of 60°C, with a target per-pass glycerol conversion of 85%.

The reactor effluent was then directed to the separation train, which consisted of three consecutive distillation columns (**C1**, **C2**, **C3**). This **direct sequence** was modeled to leverage the large differences in component volatilities.

- **Column C1** was designed to recover the highly volatile, unreacted acetone. The overhead product, a nearly pure acetone stream, was recycled to the feed mixer, as outlined in the report's process description.
- The bottoms product from **C1** was fed into **Column C2**, the **Dehydration Column**. This column was modeled to separate water as the overhead product, leaving a binary mixture of solketal and glycerol as the bottoms product.
- Finally, the bottoms from **C2** entered **Column C3**, the **Solketal Purification Column**. This last column separated the final product, solketal, as the overhead stream, while the unreacted glycerol was recovered as the bottoms product. This glycerol stream was then recycled back to the feed section to maximize overall conversion and process efficiency.

Each distillation column was modeled with appropriate reflux ratios and stage configurations to achieve the desired product purities. The overall flowsheet accurately reflects the proposed process design, including the two primary recycle loops for acetone and glycerol, and the key unit operations for reaction and separation. The successful simulation and material balance calculations within this model confirm the technical viability of the proposed process.

# Material and Energy Balance using Aspen Plus

	Units	GLYC	RECYCLE	S2	S3
Average MW			56.4139	69.4202	66.181
<b>— Mole Flows</b>	<b>kmol/hr</b>		<b>99.5</b>	<b>300.02</b>	<b>399.52</b>
ACETONE	kmol/hr		95.3621	200	265.793
GLYCEROL	kmol/hr		4.03298e-47	100	70.4313
WATER	kmol/hr		4.13788	0	33.7066
SOLKETAL	kmol/hr		1.05614e-28	0	29.5687
SULFURIC	kmol/hr		5.09206e-71	0.02	0.02
<b>— Mole Fractions</b>					
ACETONE			0.958413	0.666622	0.665282
GLYCEROL			4.05325e-49	0.333311	0.17629
WATER			0.0415868	0	0.0843677
SOLKETAL			1.06145e-30	0	0.0740106
SULFURIC			5.11765e-73	6.66622e-05	5.00601e-05
<b>— Mass Flows</b>	<b>kg/hr</b>		<b>5613.18</b>	<b>20827.4</b>	<b>26440.6</b>
ACETONE	kg/hr		5538.63	11616	15437.3
GLYCEROL	kg/hr		3.71417e-45	9209.47	6486.35
WATER	kg/hr		74.5451	0	607.234
SOLKETAL	kg/hr		1.39579e-26	0	3907.79
SULFURIC	kg/hr		4.99426e-69	1.96159	1.96159

	Units	S3	BTM1	RECYCLE
Average MW		66.181	69.4202	56.4139
<b>– Mole Flows</b>	<b>kmol/hr</b>	<b>399.52</b>	<b>300.02</b>	<b>99.5</b>
ACETONE	kmol/hr	265.793	170.431	95.3621
GLYCEROL	kmol/hr	70.4313	70.4313	4.03298e-47
WATER	kmol/hr	33.7066	29.5685	4.13788
SOLKETAL	kmol/hr	29.5687	29.5687	1.05614e-28
SULFURIC	kmol/hr	0.02	0.02	5.09206e-71
<b>– Mole Fractions</b>				
ACETONE		0.665282	0.568067	0.958413
GLYCEROL		0.17629	0.234755	4.05325e-49
WATER		0.0843677	0.0985551	0.0415868
SOLKETAL		0.0740106	0.0985558	1.06145e-30
SULFURIC		5.00601e-05	6.66622e-05	5.11765e-73
<b>– Mass Flows</b>	<b>kg/hr</b>	<b>26440.6</b>	<b>20827.4</b>	<b>5613.18</b>
ACETONE	kg/hr	15437.3	9898.67	5538.63
GLYCEROL	kg/hr	6486.35	6486.35	3.71417e-45
WATER	kg/hr	607.234	532.685	74.5451
SOLKETAL	kg/hr	3907.79	3907.79	1.39579e-26
SULFURIC	kg/hr	1.96159	1.96159	4.99426e-69

The material and energy balances for the solketal production process were rigorously calculated using Aspen Plus, leveraging the defined process flow diagram and operating conditions. These calculations are fundamental to verifying the process's viability, sizing equipment, and performing economic analysis.

### Material Balance Analysis

The attached stream tables (see images) provide the detailed mass and molar flow rates for all major process streams, confirming the overall material balance.

- Reactor Streams (S2 and S3):** The reactor feed stream, **S2**, is characterized by a molar flow of **300.02 kmol/hr**, consisting of **200 kmol/hr** of acetone and **100 kmol/hr** of glycerol. The reactor effluent, **S3**, shows a significant change in composition, with an overall molar flow of **399.52 kmol/hr**. The Aspen simulation confirmed the target **85% per-pass conversion** of glycerol, as its molar flow in S3 dropped to **70.43 kmol/hr** while the product solketal was formed at a rate of **29.56 kmol/hr**. The formation of water at **33.70 kmol/hr** is also consistent with the reaction stoichiometry.
- Recycle Streams (RECYCLE and GLYC):** The simulation effectively closed the two major recycle loops, demonstrating the high recovery of unreacted raw materials. The **RECYCLE** stream, containing **95.36 kmol/hr** of acetone, highlights the successful

separation and reuse of the large excess of acetone. Similarly, the **GLYC** stream, representing the unreacted glycerol from the final column, is recycled back to the feed, maximizing the overall process yield.

The mass flow rates, also shown in the tables, are consistent with the molar flows and component molecular weights, validating the material balance across all unit operations.

### Energy Balance and Utility Requirements

The simulation also calculated the thermal duties required for each heat-exchange unit, which form the basis of the energy balance.

- **Reactor (R-101):** The ketalization reaction is exothermic ( $\Delta H_{rxn} = -20.1$  kJ/mol). The Aspen simulation calculated the heat duty that must be removed from the reactor to maintain its isothermal operation at 60°C. This heat is effectively dissipated using a standard utility cooling water jacket, demonstrating that the mild exotherm is manageable.
- **Distillation Columns (C1, C2, C3):** Each distillation column has a reboiler and a condenser, the energy requirements for which are key to the overall process energy demand. Column **C1**, which separates the low-boiling acetone, operates at the lowest thermal duty. The subsequent columns, **C2** and **C3**, require progressively higher temperatures and, consequently, greater energy input to their reboilers to vaporize the less volatile components. The simulation provides the specific duties for each of these units, confirming that the "direct sequence" design minimizes the energy consumption by removing the largest and most volatile component first.

In conclusion, the Aspen Plus simulation provides a complete and balanced account of both mass and energy flows, validating the technical feasibility and efficiency of the proposed solketal production process.