DESIGN OF A PLANT TO PRODUCE 20,000 LITRES/DAY OF CITRIC ACID FROM CORN COB USING ASPERGILLUS *NIGER*

ABSTRACT

There has been a considerable interest in utilizing natural agricultural waste materials for the creation of value-added products, such as citric acid, as a more environmentally friendly substitute for sugar molasses. This report describes the plan for a facility that can produce 20,000 liters of citric acid per day by employing Aspergillus*niger* to convert corn cob, which is a rich source of lignocellulosic material containing cellulose, hemicellulose, and lignin. These components can be broken down into fermentable sugars for the production of citric acid through submerged fermentation using the fungus Aspergillus*niger*. This particular technology was selected as the most suitable option, yielding citric acid as the primary product and dry distillery grain as a secondary product. To fulfill the design objective of ensuring high-quality citric acid while minimizing operational, capital, and maintenance costs, and maximizing profit, the plant is designed to produce 20,000 liters of citric acid and 19,942.32 kg of dry distillery grain per day. This requires a daily input of 29,376.30 kg of corn cob and 33,716.85 kg of water. The energy balance indicates that the process is exothermic, generating 4.510 MW of power. The proposed plant design offers a sustainable and cost-effective approach to producing citric acid from corn cob using Aspergillus*niger*.

Keywords: Citric acid, corn cob, Aspergillus*niger*, design.

1. INTRODUCTION

Citric acid is a commonly employed substance in the food and beverage industry, serving as a vital food additive and industrial chemical [1]. It is renowned for its characteristic sour taste and finds widespread application as a flavor enhancer, preservative, and chelating agent. Citric acid plays a role in improving the flavor of carbonated beverages, fruit juices, and various other drinks within the food industry [2]. Additionally, it finds application in the manufacturing of jams, jellies, and candies, contributing to their production processes [3]. Citric acid finds utility in the industrial realm for its applications in cleaning and laundry detergents, metal finishing processes, and as a chelating agent employed in water treatment[1][4]. The food and beverage industry has witnessed a notable demand rise for citric acid over the recent years, primarily attributed to its versatile applications [2]. However, the conventional approaches to citric acid production rely on non-renewable fossil fuels and deplete natural resources, rendering them unsustainable[2][5]. Furthermore, there is a pressing need to explore alternative, sustainable and eco-friendly methods of citric acid production [6].

A viable alternative approach involves utilizing corn cob as a raw material for citric acid production [7]. Corn cob, an abundant and cost-effective agricultural waste, can be employed for this purpose [8]. Comprising cellulose, hemicellulose and lignin, corn cob can be enzymatically hydrolyzed to convert these components into sugars[3][9]. Subsequently, microorganisms such as Aspergillus*niger* can ferment these sugars, yielding citric acid as a byproduct [4][10].

The plant design encompasses various crucial elements, including the fermentation vessel, recovery and purification system, and process control and monitoring system [5][11]. The fermentation vessel is specifically designed to create an adequate and optimal environment for the growth and metabolic activities of Aspergillus*niger*[12], while the recovery and purification system is developed to effectively separate and purify the citric acid from the fermentation broth. The process control and monitoring system play a vital role in ensuring the smooth operation of the process and attaining the desired product quality. It also incorporates safety measures to safeguard both the workers and the environment[6][13].In essence, the primary objective of this plant design is to attain substantial citric acid production while simultaneously reducing expenses and environmental repercussions [14]. The utilization of corn cob as a feedstock and Aspergillus*niger* as the fermentation organism represents both economically viable and environmentally sustainable options. The plant is meticulously engineered to operate efficiently, minimizing waste generation[7][15].

In this research, our aim is to propose the design of a plant capable of generating 20,000 litres of citric acid per day from corn cob using Aspergillus*niger*. This citric acid holds potential applications across various industries, including food and beverage, pharmaceuticals, and detergents. The establishment of this plant is anticipated to play a crucial role in meeting the escalating demand for citric acid in these sectors, while concurrently advancing the development of a more sustainable and cost-effective citric acid production process. The plant design will involve careful selection of the suitable microorganism, optimization of the fermentation process, and formulation of a downstream processing strategy to purify and concentrate the citric acid. To assess the feasibility of the proposed plant, a series of experiments and simulations will be conducted.

1.1 CORN COB BIOMASS

Corn stands as one of the most widely cultivated cereal crops, with a global production of 885.3 million tonnes in 2014. The United States takes the lead as the foremost producer with 313.9 million tonnes, closely followed by China. India holds the sixth position in corn production [16].

Figure 1. Bare corn cob

After removing the grains, corncob remains as a material that has traditionally been utilized as feedstock or fuel, as depicted in Figure 1. It comprises hemicelluloses, cellulose, and lignin. Despite the fact that polymeric fibers are made up of monomer molecules, cellulose primarily consists of C6 sugars, while hemicelluloses consist of C5 sugars such as xylose and arabinose. However, in most cases, cellulose, hemicellulose, and lignin found in plant-derived biomass are intertwined in a complex matrix that exhibits significant resistance to enzymatic degradation [17]. Consequently, the identification of an appropriate technique for effectively utilizing the available cellulose and hemicellulose within corncob biomass remains a substantial challenge. Typically, plant biomass contains valuable industrial value-added metabolites such as glucose, xylose, acetate, furfural, hydroxymethyl furfural, and lignin [18]. Moreover, lignin can be transformed into valuable co-products such as vanillin, phenols, and high-octane hydrocarbon materials. The utilization of corncob biomass is recognized as a significant resource for obtaining these metabolites [19]. Additionally, the bioconversion of these available metabolites through microbial fermentation represents an innovative area of research. Previously, corn biomasses that were readily available were predominantly used for household combustion purposes, until the emergence of conversion technologies [19]. The latest approach for conversion involves the utilization of native and mutant strains in microbial fermentation to transform the sugars present in corncobs into valuable metabolites. This strategy encompasses various stages, including corn cob processing, acid hydrolysis, estimation of metabolites, fermentation process, consumption of substrates by selected organisms, formation of products, and quantification of both products and co-products [16].

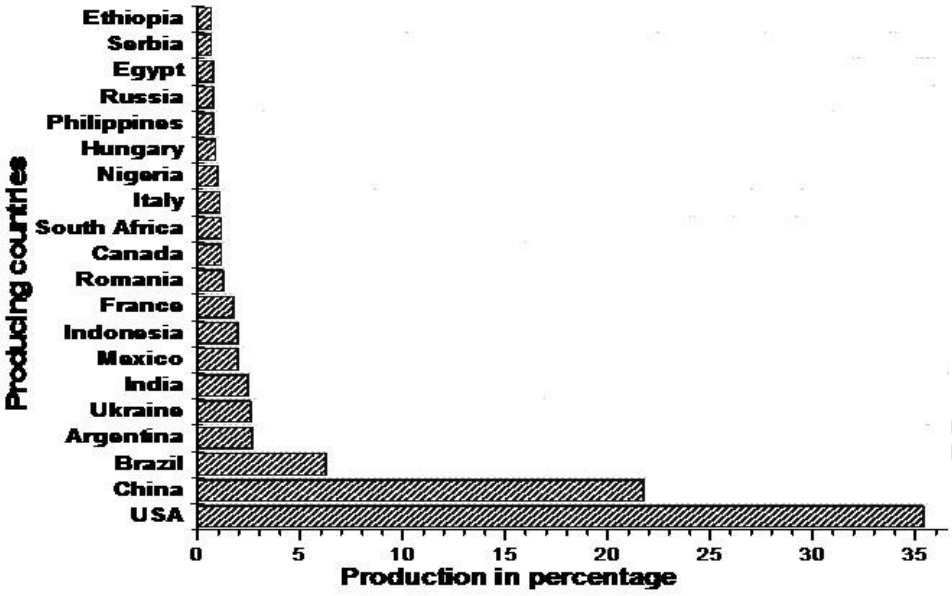

Figure 2. Worldwide Production of Corncob [8]

Plant biomass is one of the abundant waste materials in Nigeria. Within the overall biomass, corncobs constitute 40%, with only 10% of these products being used for bioconversion processes. The remaining corncob residues are traditionally employed in rural areas of Nigeria for purposes such as fire starters, pot scrubbers, and animal bedding [20]. Recently, researchers have recognized corncob biomass, the significance of its hydrolysate and valuable metabolites. These natural properties make them suitable for the production of industrial value-added products. It's important to note that there are variations in the composition of lignocelluloses depending on the source, whether it is derived from hardwood, softwood, or plants, as depicted in Figure 3.

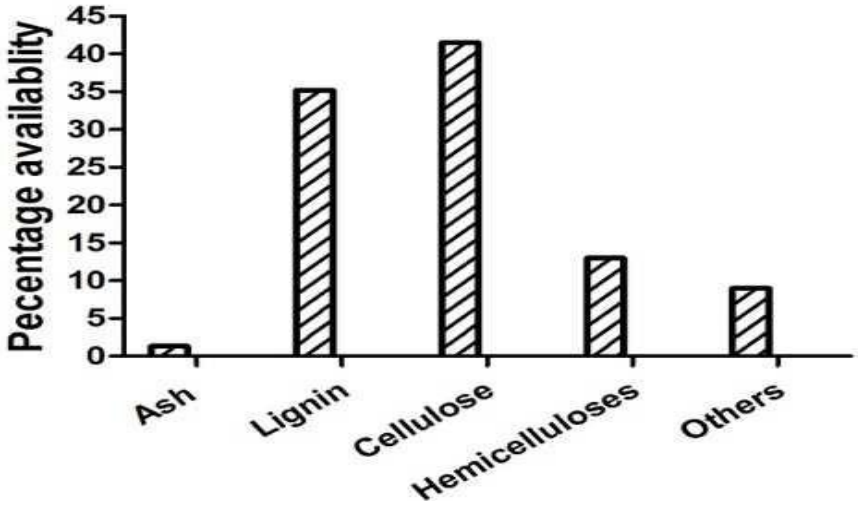

Figure 3. Corncob biomass compositions

Xylan, a complex heteroxylan found in corncob hemicelluloses, consists of ß-(1,4)-linked xylose residues [21]. It is composed of approximately 3 to 6% galactose, 6 to16% glucuronic acid, 33 to 35% arabinose and 48 to 53% xylose. Typically, about 80% of xylan can be highly substituted with arabinose or glucuronic acid'smonomeric side chains, which are connected to xylose residues at O-2 or O-3 positions. Additionally, the oligomeric side chains contains xylose, arabinose and a small amount of galactose residues [22]. Xylose, a major component of the hemicellulose hydrolysate derived from corncobs, holds significant potential for

bioconversion into xylitol, which finds a wide range of industrial applications. While chemical synthesis of xylose is feasible, it is an expensive and time-consuming process. The utilization of readily available plant biomass such as corncobs presents a promising natural resource for cost-effective and time-efficient production of xylose in large quantities. Commercial production of xylitol is typically achieved through aerobic fermentation of corncob hydrolysate using yeast species such as Debaryomyceshanseni and Debaryomycesnepalensis. Xylitol serves various purposes, including use as an artificial sweetener and in dental applications [16].

1.2 CITRIC ACID BIOCHEMISTRY

The process of citric acid production is intricate. The various nutritional elements in the medium interact with each other, impacting the quantity of citric acid generated [23]. The nutritional conditions, including concentration of the carbon source, dissolved oxygen levels, ions of hydrogen, as well as insufficient levels of phosphate and trace metals, collaborate to influence the citric acid yield. Multiple studies suggest that limiting the nitrogen source or experiencing deficiencies in phosphate or manganese in the fermentation medium can impede the A. nigeranabolism process. This obstruction can lead to protein degradation, resulting in an increased ammonium ions concentration [24].

A. niger possesses the capacity to generate abundant quantities of citrate via a highly efficient glycolytic pathway (illustrated in Figure 4). The role of citrate as an inhibitor of glycolysis has garnered considerable research interest in this regard.

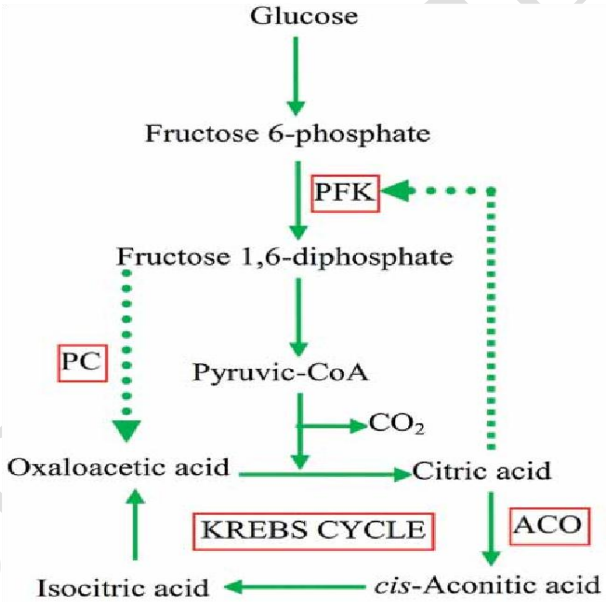

Figure 4. Schematic representation of the main metabolic reactions involved in the production of citric acid by Aspergillus*niger*[9].

Under specific circumstances, the suppressive effect of citrate can be diminished due to the buildup of various activators linked to the phosphofructokinase gene (PFK-1) ([23],[25]). Insufficient manganese levels result in protein degradation, causing an increase in concentration within the cell [26]. This occurrence, referred to as the "ammonium pool," restricts the activity of the enzyme phosphofructokinase, which plays a vital role in converting fructose and glucose into pyruvate. As a result, there is an enhanced flow through glycolysis, promoting the production of citric acid. Elevated levels of glucose and ammonium ions have a significant inhibitory effect on the activity of 2-oxoglutarate dehydrogenase, obstructing the breakdown of citric acid in the tricarboxylic acid (TCA) cycle [24].

Papagianni [39] conducted a research investigation on the initial stages of citric acid production by A. niger, which yielded results contradicting the conclusions reached by [24] and [26]. The earlier studies proposed that the inhibition of phosphofructokinase was not solely attributed to the presence of an internal pool of ammonium

ions. As indicated by [27], the entry of ammonium ions into cells leads to their combination with glucose, resulting in the formation of glucosamine, rather than being exclusively stored within the cell.

Therefore, it was discovered that phosphofructokinase enzyme inhibition is not influenced by the presence of the ammonium pool. Instead, this inhibition is affectef by various factors. These factors include the release of synthesized glucosamine into the fermentation broth, the low concentration of intracellular ammonium ions (approximately one-hundredth of the external pH), and the intracellular pH. To understand the impact of increased concentrations of glucose and ammonium ions within the tricarboxylic acid (TCA) cycle, further investigation is needed to explore the interaction among the enzymes phosphofructokinase, 2-oxoglutarate dehydrogenase, and glucosamine synthas[39]. In the production of citric acid in A. niger, enzymes like invertase play a critical role. Located on the cell membrane, invertase is essential for the breakdown of sucrose into glucose and fructose. These resulting components are then transported into the cell as part of the pathway leading to citric acid production, which occurs outside the cell [28]. Among the enzymes in A. niger, hexokinase is more abundant compared to others. It exhibits a higher affinity for glucose than fructose, with a ratio of 1000:1. Interestingly, citrate acts as a non-competitive inhibitor of the glucokinase enzyme. Schreferl-Kunar [30] demonstrated the use of mutations to create an A. niger strain with an increased affinity for sucrose during growth.

In the study conducted by Hayashi and Nakamura [31], it was observed that glucose oxidase stimulates A. niger to convert glucose into gluconic acid. The enzyme reaches its highest level of activity when there is an abundance of glucose and the fermentation conditions involve high aeration and low levels of other nutrients typically found in citric acid fermentation ([32], [33]). However, the effectiveness of glucose oxidase is limited due to its inactivation under acidic conditions with pH values below 3.5. This leads to a decrease in the pH of the fermentation broth as protons accumulate [34]. It is still uncertain whether gluconic acid plays a role in the subsequent synthesis of citric acid during fermentation. The process of phosphorylating fructose-6-phosphate is facilitated by phosphofructokinases (PFK1 and PFK2). PFK1 catalyzes the phosphorylation at the C1 position, resulting in the formation of fructose-1,6-bisphosphate. The activity of PFK1 is hindered by high levels of ATP, citrate, and manganese. However, activation of PFK1 can occur through the influence of byproducts generated from the PFK2 reaction, such as fructose-2,6-bisphosphate [35].

Prominent research conducted by Martin & Wilson [36] and Cleland & Johnson [37] has shown that the production of citric acid occurs via the glycolytic pathway. Aspergillus species have been known to employboth the glycolytic and pentose phosphate pathways to utilize glucose and other carbohydrates, which are vital for biosynthesis and cellular maintenance. Previous research suggested that the regulation of citric acid synthesis was influenced by pyruvate kinase. However, a recent study by Meixner-Monori [38] discovered that the isolated enzyme displayed minimal sensitivity to metabolic inhibitors. Citrate synthase acts as an enzyme that facilitates the condensation reversible reaction between oxaloacetate and acetyl coenzyme A (acetyl CoA), resulting in the formation of citrate. This reaction also involves thioester hydrolysis, [33]. The equation for this process is presented below:

$$\text{Acetyl CoA} + \text{Oxaloacetate} \leftrightarrow Citrate^{3-} + H^{+} + \text{CoA} - \text{SH} \qquad (1)$$

A. niger possesses three distinct isocitrate dehydrogenase isoenzymes that utilize different mechanisms to extract protons from isocitrate, as depicted in Figure 5. These isoenzymes include NADP+-dependent forms, with one located in the mitochondria and another in the cytoplasm, and NAD+-dependent isocitrate dehydrogenases exclusively found in the mitochondria. The NAD+-dependent enzymes are present in smaller quantities compared to the NADP+-dependent enzymes, as reported[40],[41].

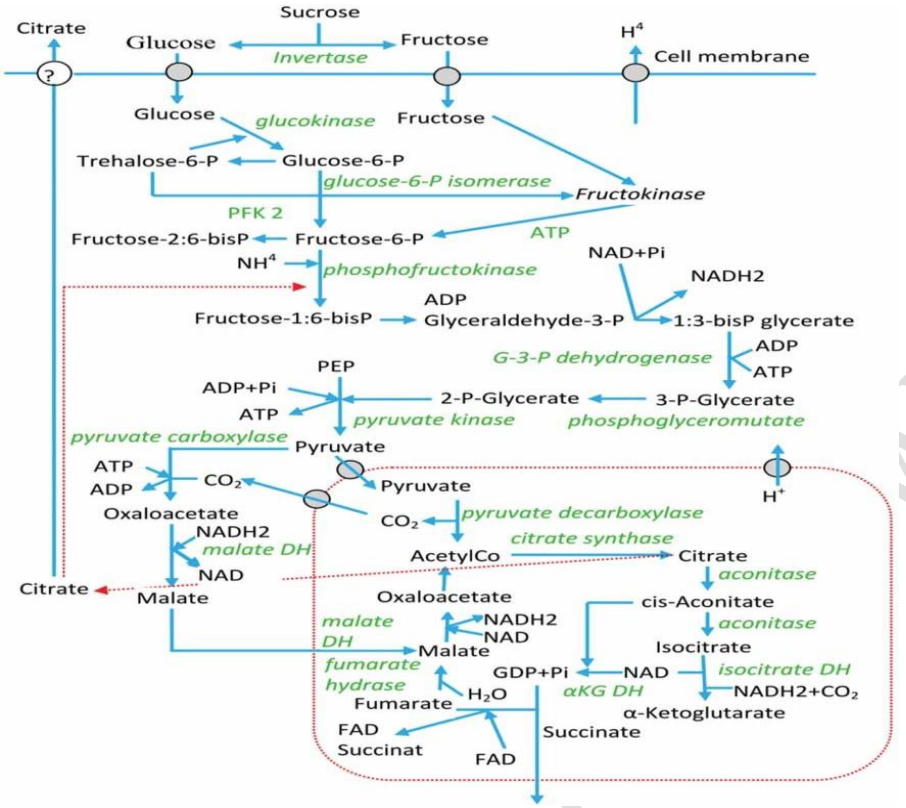

Figure 5. Schematic illustrating the metabolic reactions responsible for the synthesis of citric acid, the dashed lines indicating feedback loops as well as their locations within the cellular structure of Aspergillus*niger*[10].

1.3 FERMENTATION OF CITRIC ACID

Fermentation has emerged as the dominant and cost-effective method for citric acid production, accounting for more than 90% of global citric acid production. This approach offers several benefits, including straightforward and stable operations, simplified control systems, reduced energy consumption, and resilience against power failures at the plant [14]. Irrespective of the particular fermentation method employed, the fermentation process typically comprises three stages: preparation and inoculation, fermentation, and recovery of citric acid.

1.3.1Submerged Fermentation

Currently, the submerged fermentation technique holds the position of being the most widely adopted method worldwide. It is estimated that approximately 80% of global citric acid production is achieved through submerged fermentation [42]. This approach was developed as an advancement over surface fermentation, albeit with the requirement of more sophisticated infrastructure, increased energy consumption, and meticulous control measures to manage foam formation (which can be addressed using antifoaming agents). However, submerged fermentation offers superior productivity and higher yields, while also reducing capital, maintenance, and labor costs, and minimizing the risk of contamination. Furthermore, it demonstrates increased resilience to variations in the composition of the medium, enabling a broader selection of substrates and enhanced control over substrate utilization. This benefit facilitates the use of molasses as a medium for the production of citric acid [43]. Submerged fermentation is primarily carried out as a batch process, although continuous systems are viable and utilized in real-world applications. Submerged fermentation also involves the use of the shake flask method, which is frequently utilized to optimize fermentation conditions [44]. The shake flask method involves using an Erlenmeyer flask positioned on a shaker, with ongoing agitation throughout the fermentation procedure.

Darouneh[45] conducted a comparative study that examined different techniques for citric acid production, specifically surface and submerged culture. The findings revealed that surface fermentation yielded higher quantities of citric acid and demonstrated superior productivity compared to submerged fermentation. Ali[46] investigated citric acid production using molasses of sugarcane in a stirred fermenter, while Ikram-Ul et al.

(2004) and Khalil [47] focused on selected A. *niger*mutants capable of producing citric acid from cane molasses. Soccol[14] studied the effects of metal-complexing agents on the growth, germination, and morphology of A. niger. Roukas[34] explored the use of beet molasses as a substrate for citric acid production in shake flasks. Anastassiadis[48] examined oxygen requirements for citric acid production using Yarrowialipolytica. When designing a submerged fermenter, it is crucial to choose construction materials that can withstand the corrosive nature of low pH conditions. Austenitic stainless steel or type 316L stainless steel are commonly preferred due to their resistance to acidity. Ordinary steel and stainless steel are susceptible to corrosion in acidic environments, which can have a negative impact on citric acid production. In a comprehensive investigation conducted by Khalil et al. [47], the utilization of molasses and pumpkin as substrates for citric acid production was examined using A. niger strains 14/20 and 79/20. The study demonstrated that both substrates can effectively be used for citric acid production, with the combined substrate yielding superior overall results.

2. METHODOLOGY

2.1 PROCESS DESCRIPTION

The corn cobs feedstock is ground into a powder with a particle size ranging from 0.15 to 1 mm using a milling machine. The powdered corn cobs are then subjected to a pre-treatment process in a pre-treating unit. This involves using a 0.7% dilute sulfuric acid and steam at a pressure of 14 atm and a temperature of 190 ^{o}C for a brief period. The purpose of this pre-treatment is to release the hemicellulose sugar and other compounds present in the feedstock. After pre-treatment, the powdered feedstock is washed in a washing column. Process water is introduced into the column to remove the acid from the solids, achieving neutralization and reaching the desired pH for hydrolysis. The hydrolysate, along with enzymes, is then fed into the Hydrolyser unit, which operates at 50 ^{o}C. In this unit, both cellulose and hemicellulose undergo a conversion process into sugar, following reactions (1) and (2).

Cellulosic material $(C_6H_{10}O_5)_n$ + 2 H_2O =======> 2 Glucose (2)

Hemi cellulosic material $(C_5H_8O_4)_n$ + 2 H_2O =======> 2 Xylose (3)

The hydrolysate obtained from the hydrolyser is subjected to filtration in the Filter-1 unit, where suspended particles and impurities are separated from the hydrolysate. The resulting filtrate, or substrate, is then subjected to heat sterilization in the Sterilizer-1 unit. High-temperature steam (ranging from 120 to 170 ^{o}C) is used for a short duration to sterilize the substrate. Similarly, the nutrient and ammonium sulfate stream containing Aspergillus*niger* and ammonium sulfate are also heat sterilized in the Sterilizer-2 unit using the same quality of steam. Once sterilized, the heat-sterilized substrate and the nutrient stream containing Aspergillus*niger* are introduced into the fermentation reactor for batch fermentation, which continues for a duration of 5 days. The plant operates with 6 fermentation vessels in a staggered mode, allowing for the initiation of a new batch every 24 hours to meet the production capacity of 20,000 liters of food-grade citric acid (50 wt.%). The upstream section of the process, involving raw material preparation and fermentation, operates in batch mode.Upon completion of fermentation, the broth is transferred to a holding tank, serving as a buffer between the batch upstream section and the continuous downstream section responsible for product purification. The fermentation process occurs at an optimal temperature of 32 ^{o}C, as stated in the literature. The fermentation reaction follows the reaction (3) reported in the literature.

2 Ammonium Sulphate + 180 Glucose + 12 Nutrients + 56 O_2 ======> 16 Biomass + 30 CO_2 +154 Citric Acid + 50 H_2O (4)

The output from the fermentation vessel is transferred to a holding tank, which serves as an intermediate tank between the batch upstream process and the continuous downstream operations. This buffer tank ensures the smooth continuity of the subsequent downstream processes. From the holding tank, the product is directed to a rotary vacuum filter, also known as Filter-1. In this filtration step, the biomass/solids along with some unreacted sugar and other impurities are separated from the solution that contains citric acid.The resulting liquid solution, which contains citric acid, is then directed to the evaporator units. In these units, the solution undergoes evaporation under vacuum conditions at a temperature of 81 ^{o}C. This evaporation process reduces the water content of the solution, resulting in a concentrated liquid with an approximate citric acid concentration of 50%.

This concentration level meets the market standard for food-grade liquid citric acid with a 50 wt.% concentration.

The concentrated solution obtained from the evaporator undergoes purification by passing through an ion exchange unit. This unit operates at a temperature range of 40-45 ^{o}C and its purpose is to eliminate ions, sugar, and other impurities from the citric acid solution. Once purified, the citric acid solution, now containing more than 50 wt.% citric acid, is directed into a storage tank for the final product. Additionally, the biomass/solids that were separated from Filter-1 and Filter-2 are combined and directed to a distillery dryer known as Dryer-1. In this dryer, the solids are dried to obtain distillery grain with soluble (DGWS). The resulting DGWS serves as a byproduct of the process.The process flow diagram for the production of citric acid from corn cobs using Aspergillus*niger* is illustrated in Figure 6.

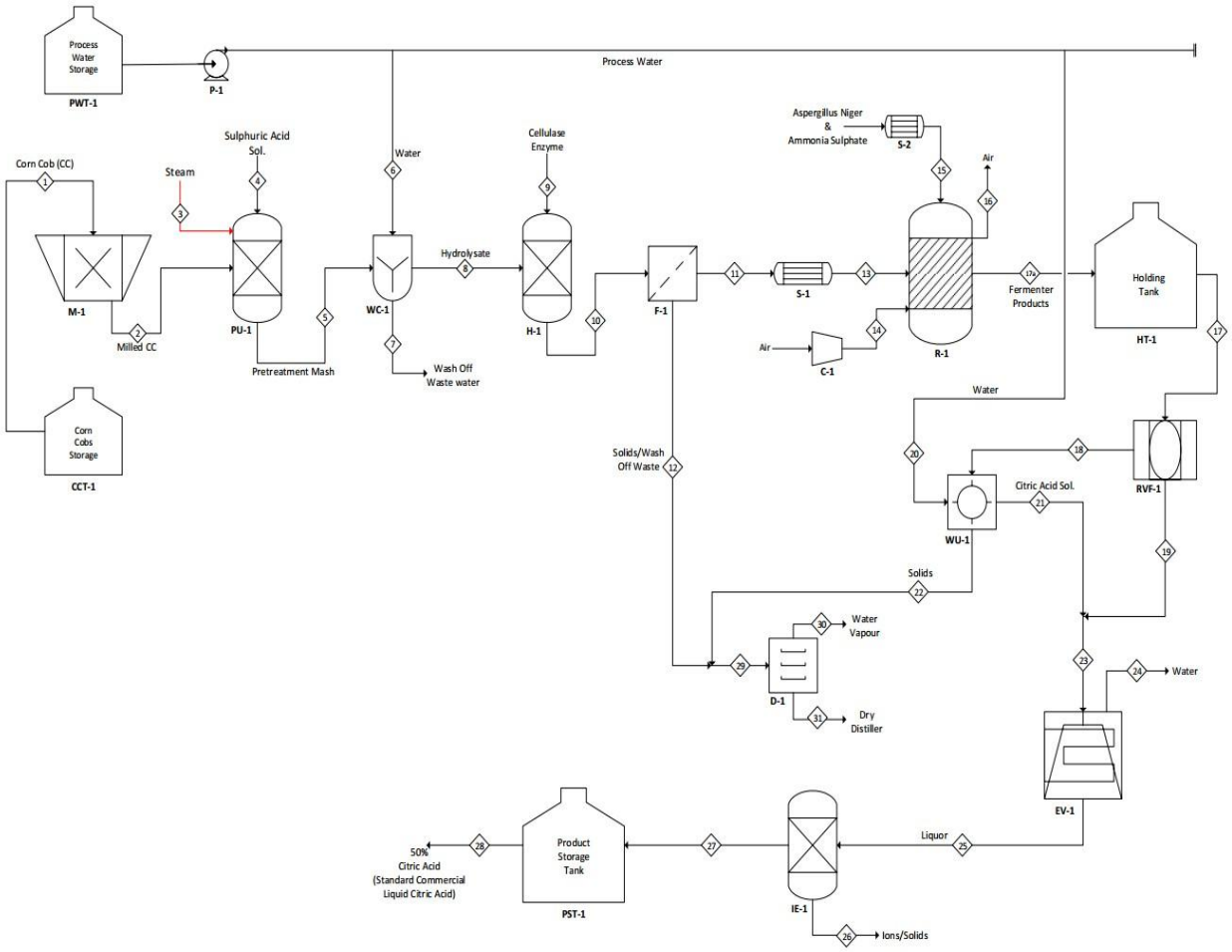

Figure 6. Process flow diagram of 20,000L/day citric acid production from corn cob using Aspergillus*niger*

2.2 MATERIAL AND ENERGY BALANCE

2.2.1 Material Balance

The material balances for the production of citric acid from corn cobs are determined for each unit operation, following the principle of mass conservation. The calculations are based on a design throughput of 20,000 liters per day of citric acid produced from corn cobs as the feedstock. The various components considered in the design include corn cobs, cellulose, hemicellulose, lignin, ash, glucose, water, sulfuric acid (H2SO4), nutrient, ammonium sulfate, carbon dioxide (CO2), biomass, G-amylase, citric acid, xylose, oxygen, and nitrogen. These components were taken into account based on the research conducted [49],[50].

General Mass Balance Equation:

Mass Output = Mass Input +Generation - Consumption – Accumulation (5)

2.2.2 Energy Balance

To assess the energy needs of the process, which involves both heating and cooling requirements, energy balance calculations were performed for several units: Pre-treatment unit, Washing Column, Hydrolyser, Sterilizer-1 and Sterilizer-2, Fermenter, Evaporator, and Dryer. The energy balance calculations were based on the following assumptions:

Steady state operation is assumed throughout:

1. Reference temperature 20 ^{o}C is utilized.
2. The influence of pressure on enthalpy is considered negligible.
3. Heat loss is for energy balance also considered negligible.

2.2.2.1 Determination of Equations for Energy Balance

The energy balance equation to be employed is expressed as follows:

$$\Delta H = n \cdot \int_{T_r}^{T_s} c_p \, dT \tag{6}$$

where

H = Enthalpy
Cp = Heat capacity
T = Temperature
n = Amount
Tr = Reference temperature
Ts = System temperature

If a reaction is involved, the equation becomes

$$\Delta H = n \cdot \int_{T_r}^{T_s} c_p \, dT + h_f \tag{7}$$

where hf = heat of formation

It should be noted that Cp is given in terms of heat capacity coefficients as

$$C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^3 \tag{8}$$

where a, b, c and d are heat capacity coefficients (constants).

So, the enthalpy balance equation will then become

$$H_i = n_i \cdot \int_{T_r}^{T} Cp_i \, dT = n_i \cdot \int_{T_r}^{T} \left(A + B \cdot T + C \cdot T^2 + D \cdot T^3 \right) dT \tag{9}$$

Integration of above equation gives

$$H_i = n_i \cdot \left(A \cdot T + \frac{B \cdot T^2}{2} + \frac{C \cdot T^3}{3} + \frac{D \cdot T^4}{4} \right) \quad (10)$$

$$H_i = n_i \cdot \left[A \cdot \left(T - T_r\right) + \frac{B \cdot \left(T^2 - T_r^{\,2}\right)}{2} + \frac{C \cdot \left(T^3 - T_r^{\,3}\right)}{3} + \frac{D \cdot \left(T^4 - T_r^{\,4}\right)}{4} \right] \quad (11)$$

The above equation is utilized for approximating the enthalpy of every stream

Were

T = Stream temperature

Tr = Reference temperature

When a Reaction Takes Place

In order to include the energy alteration resulting from a reaction (referred to as Heat of Reaction) in the energy balance, the enthalpy of each individual constituent is included as an additional factorknown asthe standard heat of formation (ΔH^o_f). The superscript 'o' represents the 'standard state' while the subscript 'f' signifies 'formation'. When considering a single species without any pressure influence on the enthalpy and no phase transition, the change in enthalpy during a reaction attemperature T can be expressed as follows:

$$H_i = n \cdot \left[\Delta Ho_f + \int_{T_r}^{T_s} \left(a + b \cdot T + c \cdot T^2 + d \cdot T^3\right) dT \right] \quad (12)$$

The equation is similarly utilized to compute the change in enthalpy of all other species participating in the reaction,including those present in the product.

Consequently, the enthalpy changes across the input and output stream (Energy Input and output) is thus;

2.2.2.2 Energy Input

The overall energy supplied to a system is determined by the sum of the enthalpies of all components within the input stream, considering their respective temperatures at the input.

$$\Delta H_{input} = \sum \left(H_1 + H_2 + H_3 + ----------H_n\right) \quad (13)$$

2.2.2.3 Energy Output

The overall energy output released by a system is equal to the sum of the enthalpies of all components in the output stream, considering their respective temperatures at the output.

$$\Delta H_{output} = \sum \left(H_1 + H_2 + H_3 + ----------H_n\right) \quad (14)$$

Thus, the thermal energy (duty) required for a particular unit operation can be determined by the difference between the total enthalpies of the input and output streams. This is represented as,

Duty (Q) = Total Enthalpy of products - Total Enthalpy of Reactants

Duty (Q) = Total Output Enthalpy - Total Input Enthalpy (15)

2.2.3 Energy Balance Calculations

Determination of enthalpies of various species: the reference state is the elements at 20 ^{o}C.

$T_r := 20°C = 293.15K$

$$h(s,\theta) = n_{s,1}\cdot\left[\begin{array}{l}\frac{c_{s,0}}{1}\cdot\left(T - T_r\right) + \frac{c_{s,1}}{2}\cdot\left(T^2 - T_r{}^2\right) \ldots \\ + \frac{c_{s,2}}{3}\cdot\left(T^3 - T_r{}^3\right) + \frac{c_{s,3}}{4}\cdot\left(T^4 - T_r{}^4\right)\end{array}\right]\cdot\frac{kJ}{kg} \quad (16)$$

Employing the values gotten from the energy balance, the calculation method for determining the overall energy needed for citric acid production is as follows:

$$Q_{Cooling} := Q_{washCol} + Q_{Hydrolyzer} + Q_{Fermenter} + Q_{IonExchang} \quad (17)$$

$$Q_{Heating} := Q_{pretreatment} + Q_{Sterilizer1} + Q_{Sterilizer2} + Q_{Evaporator} + Q_{Dryer} \quad (18)$$

For the total energy of the process QT = Q heating + Q cooling (19)

3. RESULTS AND DISCUSSION

3.1 Material Balance across the plant

The overall material balance calculation across the individual unit operations that makes up the entire process was summarized in Table 1.

Table 1: Summary of the overall material balance across the process

Component	Input Stream (kg/batch) Stream 1, 3, 4, 6, 9, 14, 15 and 20	Output Stream (kg/batch) Stream 7, 16, 24, 30, 31, 26, 28
Corn Cobs	29376.30	0
Cellulose	0.00	264.38
Hemicellulose	0.00	8460.36
Lignin	0.00	4993.98
Ash	0.00	1762.58
Glucose	0.00	429.04
Water	66394.27	65211.76
H2SO4	226.20	223.934
Nutrient	212.64	5.88
Ammonium Sulphate	170.11	56.28
CO2	0.00	568.699
Biomass	0.00	1361.48
G-Amylase	1468.82	1468.82
Citric Acid	0.00	12744.32

Xylose	0.00	1068.2
Oxygen	782.50	10.854
Nitrogen	2619.67	2619.668
Total	101250.49	101250.49

3.2 Energy Balance across the Plant

The summary of energy balance calculations across the unit operations involving energy generation or consumption are presented in Table 2 – 10.

Table 2: Summary of energy balance across corn cobs pre-treatment unit

	Input Stream (kJ/batch)			Output Stream (kJ/batch)
Component	Stream 2	Stream 3	Stream 4	Stream 5
Corn Cobs	192591.008	0.000	0.000	0.000
Cellulose	0.000	0.000	0.000	2721239.565
Hemicellulose	0.000	0.000	0.000	2085482.134
Lignin	0.000	0.000	0.000	1309119.460
Ash	0.000	0.000	0.000	276567.313
Glucose	0.000	0.000	0.000	0.000
Water	0.000	2850357.194	208926.314	10093114.825
H2SO4	0.000	0.000	1051.388	38588.895
Nutrient	0.000	0.000	0.000	0.000
Ammonium Sulphate	0.000	0.000	0.000	0.000
CO2	0.000	0.000	0.000	0.000
Biomass	0.000	0.000	0.000	0.000
G-Amylase	0.000	0.000	0.000	0.000
Citric Acid	0.000	0.000	0.000	0.000
Xylose	0.000	0.000	0.000	0.000
Oxygen	0.000	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000	0.000
Total	192591.008	2850357.194	209977.702	16524112.192

Duty = H5 – (H2 + H3 + H4) = 16524112.192 – (192591.008 + 2850357.194 + 209977.702)

= 13271186.287 kJ/batch

Table 3: Summary of energy balance across washing column

	Input Stream (kJ/batch)		Output Stream (kJ/batch)	
Component	Stream 5	Stream 6	Stream 7	Stream 8
Corn Cobs	0.000	0.000	0.000	0.000
Cellulose	2721239.565	0.000	0.000	576262.496
Hemicellulose	2085482.134	0.000	0.000	441631.511
Lignin	1309119.460	0.000	0.000	277225.297
Ash	276567.313	0.000	0.000	58214.511
Glucose	0.000	0.000	0.000	0.000
Water	10093114.825	283666.188	2076373.103	2076373.103
H2SO4	38588.895	0.000	7545.569	153.991
Nutrient	0.000	0.000	0.000	0.000
Ammonium Sulphate	0.000	0.000	0.000	0.000
CO2	0.000	0.000	0.000	0.000
Biomass	0.000	0.000	0.000	0.000
G-Amylase	0.000	0.000	0.000	0.000
Citric Acid	0.000	0.000	0.000	0.000
Xylose	0.000	0.000	0.000	0.000
Oxygen	0.000	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000	0.000
Total	16524112.192	283666.188	2083918.672	3429860.909

Duty = (H7 + H8) – (H5 + H6) = (3429860.909 + 2083918.672) – (283666.188 + 16524112.192)

= –11293998.799 kJ/batch

Table 4: Summary of energy balance across hydrolyser unit

	Input Stream (kJ/hr)		Output Stream (kJ/hr)
Component	Stream 8	Stream 9	Stream 10
Corn Cobs	0.000	0.000	0.000
Cellulose	576262.496	0.000	-1325820.256
Hemicellulose	441631.511	0.000	-56607094.374
Lignin	277225.297	0.000	-52229460.289
Ash	58214.511	0.000	-19903207.753
Glucose	0.000	0.000	-100472361.603
Water	2076373.103	-19616462.092	-410092833.956
H2SO4	153.991	0.000	-5860.272

Nutrient	0.000	0.000	0.000
Ammonium Sulphate	0.000	0.000	0.000
CO2	0.000	0.000	0.000
Biomass	0.000	0.000	0.000
G-Amylase	0.000	-6561783.642	-6561783.642
Citric Acid	0.000	0.000	0.000
Xylose	0.000	0.000	-7458697.966
Oxygen	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000
Total	3429860.909	-26178245.734	-654657120.111

Duty = H10 – (H8 + H9) = – 654657120.111 – (3429860.909 + -26178245.734)

= – 631908735.286 kJ/hr

Table 5: Summary of energy balance across substrate sterilizer (Sterilizer-1)

	Input Stream (kJ/batch)	Output Stream (kJ/batch)
Component	Stream 11	Stream 13
Corn Cobs	0.000	0.000
Cellulose	230.505	320.146
Hemicellulose	7949.367	11040.788
Lignin	2772.253	3850.351
Ash	582.145	809.049
Glucose	1270003.805	1763894.174
Water	1862725.432	2591195.484
H2SO4	76.996	107.716
Nutrient	0.000	0.000
Ammonium Sulphate	0.000	0.000
CO2	0.000	0.000
Biomass	0.000	0.000
G-Amylase	7535.02	10465.306
Citric Acid	0.000	0.000
Xylose	13750.591	19098.043
Oxygen	0.000	0.000
Nitrogen	0.000	0.000

Total	3165626.114	4400781.058

Duty = H13 – H11 = 4400781.058 – 3165626.114 = 1235154.943 kJ/batch

Table 6: Summary of energy balance across nutrient sterilizer (Sterilizer-2)

	Input Stream (kJ/batch)	Output Stream (kJ/batch)
Component	Inlet Stream	Stream 15
Corn Cobs	0.000	0.000
Cellulose	0.000	0.000
Hemicellulose	0.000	0.000
Lignin	0.000	0.000
Ash	0.000	0.000
Glucose	0.000	0.000
Water	0.000	0.000
H2SO4	0.000	0.000
Nutrient	4231.444	42314.445
Ammonium Sulphate	931.428	9314.281
CO2	0.000	0.000
Biomass	0.000	0.000
G-Amylase	0.000	0.000
Citric Acid	0.000	0.000
Xylose	0.000	0.000
Oxygen	0.000	0.000
Nitrogen	0.000	0.000
Total	5162.873	46465.853

Duty = H15 – H_{feed} = 51628.726 – 5162.873 = 71009.380 kJ/batch

Table 7: Summary of energy balance across fermentation unit

	Input Stream (kJ/batch)			Output Stream (kJ/batch)	
Component	Stream 13	Stream 14	Stream 15	Stream 16	Stream 17A
Corn Cobs	0.000	0.000	0.000	0.000	0.000
Cellulose	-26426.764	0.000	0.000	0.000	-26670.075

Hemicellulose	-1129050.467	0.000	0.000	0.000	-1137441.466
Lignin	-521216.505	0.000	0.000	0.000	-524142.772
Ash	-198805.173	0.000	0.000	0.000	-199420.386
Glucose	-98973747.618	0.000	0.000	0.000	-2006286.144
Water	-368355080.509	0.000	0.000	0.000	-375526251.649
H2SO4	-2899.416	0.000	0.000	0.000	-2981.799
Nutrient	0.000	0.000	-929429.335	0.000	-26592.953
Ammonium Sulphate	0.000	0.000	-1510898.495	0.000	-502152.94
CO2	0.000	0.000	0.000	-5082773.652	0.000
Biomass	0.000	0.000	0.000	0.000	10700163.546
G-Amylase	-325158.896	0.000	0.000	0.000	-333112.529
Citric Acid	0.000	0.000	0.000	0.000	-102225920.365
Xylose	-2232261.938	0.000	0.000	0.000	-2246776.451
Oxygen	0.000	-4088404.919	0.000	-56641.833	0.000
Nitrogen	0.000	44218764.636	0.000	44237832.666	0.000
Total	-471764647.285	40130359.7171	-2440327.8303	39098417.181	-474057585.9812

Duty = (H16 + H17) – (H13 + H14 + H15) = -434959168.8 – (-434074615.399)

= – 884553.401 kJ/batch

Table 8: Summary of energy balance across evaporator per hr basis

	Input Stream (kJ/hr)	Output Stream (kJ/hr)	
Component	Stream 23	Stream 24	Stream 25
Corn Cobs	0.000	0.000	0.000
Cellulose	0.051	0.000	0.391
Hemicellulose	1.767	0.000	13.47
Lignin	0.616	0.000	4.697
Ash	0.129	0.000	0.988
Glucose	270.934	0.000	2065.873
Water	20733.127	79512.98	79512.98
H2SO4	0.000	0.000	0.000
Nutrient	0.936	0.000	7.138
Ammonium Sulphate	6.902	0.000	52.627
CO2	0.000	0.000	0.000

Biomass	13638.982	0.000	112508.134
G-Amylase	8.372	0.000	63.838
Citric Acid	5950.123	0.000	45369.688
Xylose	29.029	0.000	221.346
Oxygen	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000
Total	40640.968	79512.98	239821.17

Duty = (H24 + H25) – H23 = (79512.98 + 239821.17) – (40640.968) = 278693.182 kJ/hr

Table 9: Summary of energy balance across ion exchange unit

	Input Stream (kJ/hr)	Output Stream (kJ/hr)	
Component	Stream 25	Stream 26	Stream 27
Corn Cobs	0.000	0.000	0.000
Cellulose	0.391	0.154	0.000
Hemicellulose	13.47	5.300	0.000
Lignin	4.697	1.848	0.000
Ash	0.988	0.388	0.000
Glucose	2065.873	487.681	325.121
Water	79512.98	4673.095	26480.872
H2SO4	0.000	0.000	0.000
Nutrient	7.138	2.809	0.000
Ammonium Sulphate	52.627	20.706	0.000
CO2	0.000	0.000	0.000
Biomass	112508.134	41927.828	0.000
G-Amylase	63.838	25.117	0.000
Citric Acid	45369.688	178.504	17671.865
Xylose	221.346	78.378	8.709
Oxygen	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.000
Total	239821.17	47401.807	44486.567

Duty = (H24 + H25) – H23 = (47401.807 + 44486.567) – (239821.17)

= – 147932.797 kJ/hr

Table 10: Summary of energy balance across distillery dryer

	Input Stream (kJ/hr)	Output Stream (kJ/hr)	
Component	Stream 29	Stream 30	Stream 31
Corn Cobs	0.000	0.000	0.000
Cellulose	240.013	0.000	2080.116
Hemicellulose	8277.279	0.000	71736.414
Lignin	5774.372	0.000	50044.557
Ash	1211.401	0.000	10553.59
Glucose	288.423	0.000	2499.67
Water	9298.972	77589.721	4083.67
H2SO4	1.586	0.000	14.527
Nutrient	15.798	0.000	136.915
Ammonium Sulphate	33.277	0.000	288.4
CO2	0.000	0.000	0.000
Biomass	1266625.694	0.000	12905866.429
G-Amylase	3123.894	0.000	27073.747
Citric Acid	112.692	0.000	976.662
Xylose	900.473	0.000	7804.097
Oxygen	0.000	0.000	0.000
Nitrogen	0.000	0.000	0.004
Total	1295903.8736	77589.721	13083158.7931

Duty = (H30 + H31) – H29 = (77589.721 + 13083158.7931) – (1295903.8736)

= 11864844.64 kJ/hr

DISCUSSION

The process flow diagram was created using Visio, and calculations were performed using Mathcad software. Material and energy balance calculations were conducted using species indices such as Corn Cobs, Cellulose, Hemicellulose, Lignin, Ash, Glucose, Water, H2SO4, Nutrient, Ammonium Sulfate, CO2, Biomass, G-Amalyse, Citric Acid, Xylose, Oxygen, and Nitrogen. The design capacity of the citric acid plant from corn cobs using Aspergillus*niger* was set at 20,000 liters per day. Due to the specific requirements and characteristics of the process, batch operations were adopted for the hydrolysis and fermentation units. Hydrolysis takes approximately 2 days, while fermentation lasts for 5 days. For the upstream processes, the fermentation is carried out in 5 fermenters operating in staggered mode. This means that one fermentation batch is initiated and completed on a daily basis to ensure continuous operation. This allows the plant to start a new batch every 24 hours, allowing the downstream section of the process to operate continuously. A holding tank is used to store the produced fermentation batch, ensuring a continuous supply of raw citric acid solution to downstream operations. The material balance calculations for the entire plant, as shown in Table 1, indicate that a feedstock of 29,376.298 kg/day of corn cobs is required to achieve a production capacity of 20,000 liters/day of citric acid (standard food-grade citric acid with a 50 wt% concentration). The process also utilizes 33,716.845 kg/day of process water and requires a steam rate of 8,812.889 kg/day at a pressure of 14 atm andtemperature of

190°C.The energy balance calculations for the unit operations, involving energy generation or consumption, are summarized in Tables 2-10. The overall energy balance calculations for the plant reveal that the total cooling requirement is estimated to be 647,045,943.419 kJ/day, and the heating requirement is 257,423,563.535 kJ/day for a plant capacity of producing 20,000 kg/day of citric acid. The theoretical power generated from the total energy of the process is reported to be 4.510 MW, indicating that the process flow is exothermic.

4. CONCLUSION

The aim of this design project is to achieve a daily production of 20,000 liters of citric acid using corn cobs as the raw material. Considering the specific characteristics and operational requirements of the process, a continuous process is selected as the preferred method, despite involving batch processes for hydrolysis and fermentation units. To attain the desired production capacity, six fermenters are utilized in a staggered mode of operation, ensuring continuous operation with one fermentation batch initiated and completed daily. By operating the six fermenters in this manner, a new batch can be started every 24 hours. The initial stage of the process, involving raw material preparation and fermentation, operates in batch mode. Upon completion of fermentation, the resulting broth is transferred to a holding tank, acting as a buffer between the batch upstream section and the continuous downstream section. The continuous process is designed to run continuously, 24/7, throughout the year. The design aims to produce high-quality citric acid while minimizing operational, capital, and maintenance costs and maximizing profitability. The plant is designed to produce 20,000 liters of citric acid and 19,942.32 kg of dry distillery grain per day. This necessitates a daily input of 29,376.30 kg of corn cobs and 33,716.85 kg of water. The proposed plant design offers a sustainable and cost-effective solution for citric acid production from corn cobs using Aspergillus*niger*. It is expected to meet the growing demand for citric acid in various industries and provide significant economic advantages.

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