

Article

A Graph-Based Dynamic Modeling for Palm Oil Refining Process

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Abstract: Graph theory is a well-established mathematical concept that is widely used in numerous applications such as in biology, chemistry and network analysis. The advancement in the theory of graph has led to the development of a concept called autocatalytic set. In this paper, a mathematical modeling technique namely graph-based dynamic modeling of palm oil refining process is introduced. The system parameters are identified in detail in the beginning of the paper. The parameters involved are the chemical compounds used or produced during the refining process. These identified parameters are then modeled as the vertices and edges of the graph. The dynamicity of the system is then simulated and analyzed. The system is simulated using MATLAB software programming. The two final products produced by the refining process agreed with results obtained from other published methods. Hence, the effectiveness and simplicity of the model are established.

Keywords: autocatalytic set; crude palm oil; dynamic system; modeling; refining process



Citation: Ashaari, A.; Ahmad, T.; Awang, S.R.; Shukor, N.A. A Graph-Based Dynamic Modeling for Palm Oil Refining Process. *Processes* **2021**, *9*, 523. <https://doi.org/10.3390/pr9030523>

Academic Editor: Farid B. Cortés

Received: 31 January 2021

Accepted: 9 March 2021

Published: 13 March 2021

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1. Introduction

The refining of palm oil improves the production of palm oil and its quality. It is a process to extract oil from crude palm oil (CPO) into an edible form. Before the refining process is conducted, CPO needs to be extracted from palm oil fruits. Figure 1 illustrates the production stages for CPO.

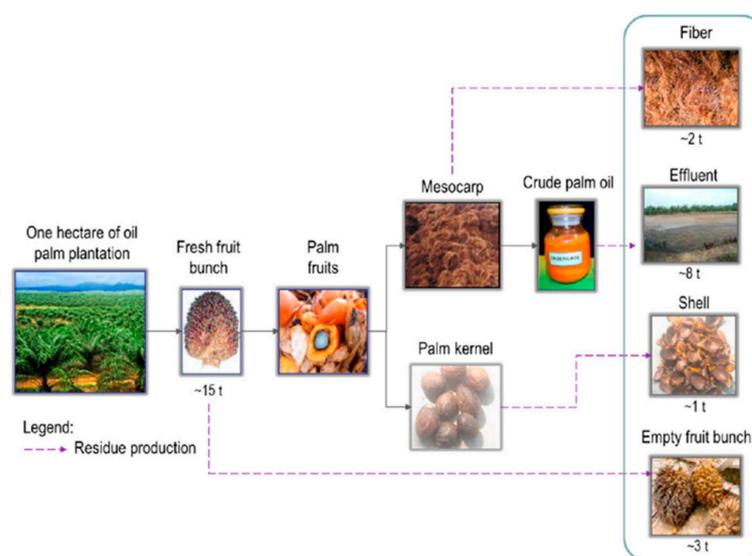


Figure 1. Flow of crude palm oil production [1].

There are two types of refining processes, namely, chemical and physical [2]. Chemical compounds are used in former. On the other hand, less harmful elements and procedures are utilized for later. However, as time passed, the use of chemicals has been reduced due to its cost, time needed for processing, and its ill-effect when consumed by humans. As a result, physical-based refining was introduced at the end of the 1970s as an alternative to chemical-based refining [3]. Physical-based refining requires natural materials to refine palm oil. They are bleaching earth (earth clay) and phosphoric acid. Steam (water) injection is used at the end of the process to remove free fatty acids (FFA) from the palm oil [4].

There are three processes in physical-based refining: degumming, bleaching, and deodorization. In 2006, Morad et al. [2] has presented an overview of the design for degumming and bleaching process of palm oil. Further improvement for esterification reactions involving high free fatty acid content of crude palm oil and glycerol using zinc glycerolate and zinc soap catalysts was presented in the Sriwijaya International Seminar on Energy Science and Technology in September 2011 [5]. However, in this paper, a new mathematical method, namely, autocatalytic set, is described to model the palm oil refining process. The used technique demonstrates the process which occurs during the refining process in great detail. There are no studies that have been reported in literatures that utilize such method for refining process of palm oil. The rest of the paper is written in the following sections. Section 2 describes the refining process of palm oil in general and Section 3 focuses mainly on elements with respect to physical refining process. The methodology used in this study is introduced in Section 4 and followed by Section 5. The following two sections are on the implementation of the method to the refining process of palm oil. Section 8 is on the analysis of the model and Section 9 is the conclusion of the study.

2. Refining Process

The purpose of refining is to process crude palm oil (CPO) into edible oil. Impurities and other compounds are removed during the process. Figure 2 illustrates the stages involved in palm oil manufacturing, from the plantation to the refining. Firstly, the CPO is extracted from palm fruit [6]. It consists of desirable triglycerides and unsaponifiables compounds with a small amount of impurities [7]. These impurities are then removed during the refining process because they affect the quality of palm oil, in particular, color, flavor, odor, stability and produce foams. Morad et al. [2] used neural network to model degumming and bleaching procedures of palm oil for the refining process.

Compositions of the crude palm oil (CPO) [8] can be categorized in several groups in general and listed in Table 1.

Table 1. Crude palm oil (CPO) compounds.

Group	Compounds
Oil	Triglyceride, Diglyceride, Monoglyceride, Phospholipids, Glycolipid and Lipoprotein, Free fatty acids
Oxidized Products	Peroxides, Aldehydes, Ketones, Furfurals (from sugars)
Non-oil Solubles	Carotene, Tocopherols, Squalene, Sterols
Impurities	Metal particles, Metal ions, Metal complexes
Water Solubles	Water (moisture), Glycerol, Chlorophyll pigments, Phenols, Sugars (soluble carbohydrates)

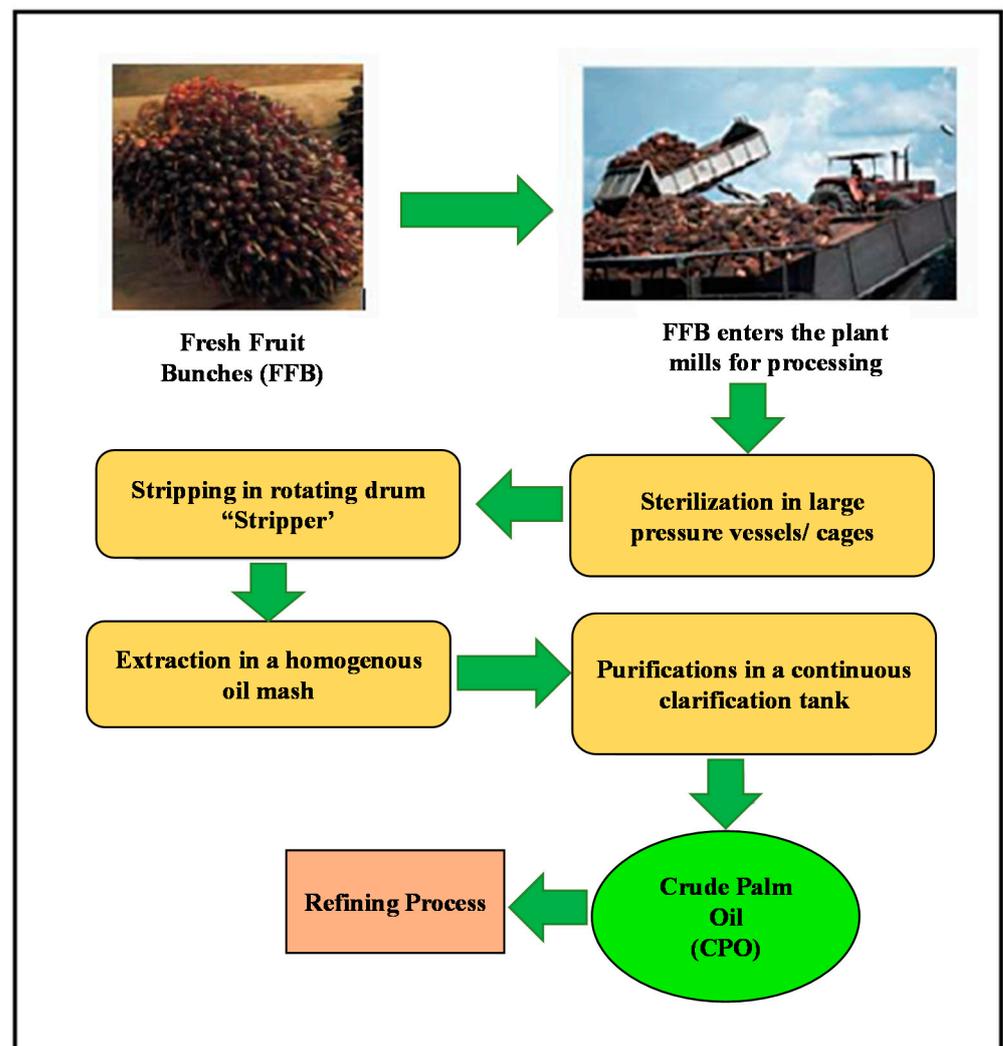


Figure 2. Palm oil refining process.

In particular, Table 2 tabulated quantitatively the amount of CPO compounds of Malaysian crude palm oil [2].

Table 2. The main compounds in Malaysian crude palm oil (CPO).

Compounds	Crude Palm Oil (CPO)
Triglycerides	95%
Free Fatty Acids, FFA	2–5%
Red Color (5 $\frac{1}{4}$ " Lovibond Cell)	Orange Red
Moisture and Impurities	0.15–3.00%
Peroxide Value, PV	1–5.0 meq/kg
Anisidine Value, AV	2–6
β -Carotene Content	500–700 ppm
Phosphorus, P	10–20 ppm
Iron (Fe)	4–10 ppm
Tocopherols	600–1000 ppm
Diglycerides	2–6%

The acceptable amount with respect to CPO in Malaysia is maximum 5% only for fatty acid and 2.5% for moisture and impurities [9]. However, the standard specification of compounds for refined palm oil gazette by Palm Oil Refiners Association of Malaysia (PORAM) are summarized in Table 3.

Table 3. PORAM (Palm Oil Refiners Association of Malaysia) standard specifications for refined palm oils.

Parameter	RBD Palm Oil
Free Fatty Acids, FFA	0.1 max (% as Palmitic)
Moisture and Impurities	0.1 max (%)
Iodine Value	50–55 (<i>Wijs</i>)
Melting Point	33–39 (OC – AOCs Cc 3 – 25)
Color	3 or 6 Red max (5.25" <i>Lovibond Cell</i>)

There are two types of palm oil refining in Malaysia: i.e., chemical and physical. Figure 3 illustrates the stages for chemical and physical refining processes of palm oil. The chemical refining process requires more stages than physical refining. Hence, the total operating costs for physical refining is expected to be smaller than chemical refining. This is due to the use of high effluent treatment in chemical refining purpose. Yusoff and Thiagarajan [10] claimed that physical refining costs less operationally and capital inputs, fewer oil losses, less influent, and greater efficiency than chemical refining. As a result, chemical refining is less adopted than physical refining in Malaysia.

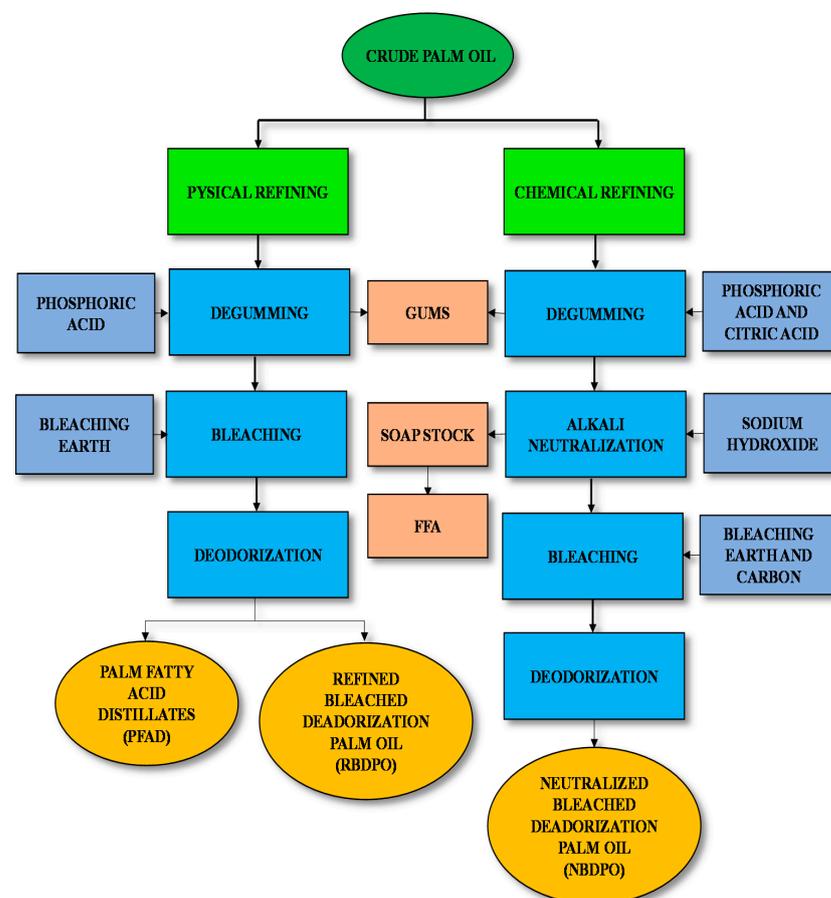


Figure 3. Chemical and physical refining process of palm oil.

In 1985, Er [11] published a guideline contents for CPO, degummed bleached palm oil (DBPO) and refined bleached deodorized palm oil (RBDPO) (see Table 4). The DBPO is the resultant from the degumming and bleaching process, and RBDPO is the final product of the refining process [11].

Table 4. Guideline contents for CPO, DBPO (degummed bleached) and RBDPO (refined bleached deodorized palm oil).

Parameters	Crude Palm Oil (CPO)	Degummed Bleached Palm Oil (DBPO)	RBD Palm Oil (RBDPO)
FFA	2–5%	3–5%	~0.05
M and I	0.15–3.0%	~0.2%	~0.02
PV	1.5–5.0	Nil	Nil
AV	2–6	2–6	2–6
β -Carotene Content	500–600 ppm	-	-
DOBI	2–3.5	-	-
Phosphorus	10–18 ppm	~4 ppm	~3 ppm
Iron (Fe)	4–10 ppm	~0.15 ppm	~0.15 ppm
Copper (Cu)	~0.05 ppm	~0.05 ppm	~0.05 ppm
Color (5.25" Lovibond Cell)	-	-	Red 2.0

Basically, both refining processes are complex multidimensional systems. However, only physical refining process is considered in this study.

3. Physical Refining

The physical refining of palm oil consists of two stages, namely, pretreatment and deodorization. Pretreatment involves degumming and bleaching processes. The aim of the process is to remove undesirable impurities. This aim is achieved when chemical compounds, phosphoric acid and bleaching earth are added in the process. These compounds are used to adsorb the unwanted impurities whereby the color, flavor, and shelf-life stability of the finished product are monitored and controlled [12]. Furthermore, high temperatures are needed to remove free fatty acids (FFA) from CPO during steam distillation in the deodorization process [4]. The schematic diagram of the process is illustrated in Figure 4. The degumming, bleaching, and deodorization processes are described in detail in the following subsections.

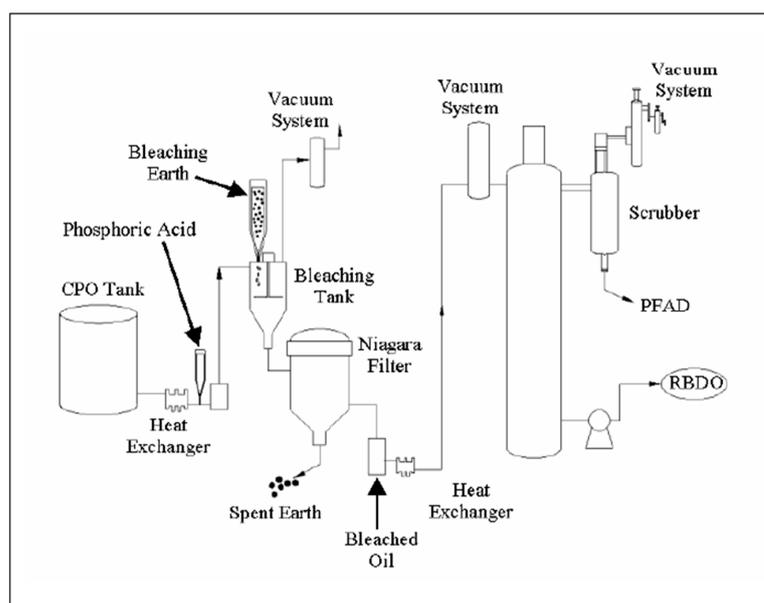


Figure 4. Physical refining process [2].

3.1. Degumming

The purpose of the degumming is to remove unwanted gum from CPO using phosphoric acid. The amount of phosphoric acid is controlled during the degumming process. This is due to the fact that excess phosphoric acid is difficult to remove, which leads to further refining problems. The unwanted phosphatide is removed during the degumming. It is essential to remove phosphatide since it affects color, flavor, and lifespan of the oil. Phosphatide is the main culprit that affects the instability of oxidation in CPO. The degumming process starts by heating the CPO to 90 °C up to 110 °C. It is then treated by phosphoric acid. The amount of phosphoric acid is 0.05% to 0.1% of palm oil weight with concentrations of 80% to 85%. The decomposed phosphatide is then removed from the CPO.

3.2. Bleaching

The CPO resultant from the degumming process is then heated to 100 °C and treated by bleaching earth. Bleaching earth is a solution that is added in ranges of 0.5% to 20% of the weight of palm oil. This mixture is then continuously blended for 30 min. The purpose of this process is to remove the other unwanted compounds and to accelerate the reaction between compounds of the mixture. Then, the CPO is filtered before being transferred to the deodorization process. Phosphoric acid, pigments, trace metals, phosphatides, and oxidation compounds are removed during deodorization.

3.3. Deodorization

The palm oil is then heated up to 240–260 °C, under vacuum (2–4 mmHg) by direct steam injection with respect to 2.5% to 4.0% of the weight of palm oil. This process is for deacidification and deodorization of the palm oil [12]. The Free Fatty Acids (FFA) are removed as palm fatty acid distillate (PFAD). The resultant products due to oxidation as well as carotenoid pigment are removed since they may affect the flavor of the oil. The final product of the deodorization is refined bleached deodorized palm oil (RBDPO). The RBDPO is then cooled and filtered before finally filled into the storage tanks.

The quality of palm oil depends on the amount of free fatty acids, moisture, heavy metals, oxidized products, and minor constituents. The details of these compounds are as follows:

Free fatty acid (FFA)

Free fatty acids (FFA) are formed when triglyceride, diglyceride, and monoglyceride are decomposed by chemical or enzymatic hydrolysis. Enzymes are used when there is a large amount of moisture in the palm oil [13]. Sometimes more than 2% FFA are produced. High FFA content must be avoided due to large refining losses and possible problems in the upcoming bleaching process [13].

Moisture

Palm oil consists of moisture. Under certain conditions, the triglyceride of palm oil is hydrolyzed into free fatty acids and glycerol [13]. However, the hydrolytic compound resultant from triglyceride molecules under 0.1% of moisture is negligible.



Therefore, in order to control the quantity of FFA, CPO must be stored with moisture content below 0.1% in order to eliminate further oxidation [9].

Heavy (trace) metals

Heavy metals or trace metals such as iron (Fe), copper (Cu), cadmium (Cd), lead (Pb), and manganese (Mn) are surrounded by phospholipids, proteins, lipids, and non-lipid compounds. The existence of trace metals due to corrosion reactions in the palm oil mill, storage and ship tanks, tankers, pipelines and refinery processes. Heavy metals are pro-oxidants that affect the quality of the palm oil. They act as catalyzers for hydro-peroxide

decompositions. Iron (Fe) increases the rate of peroxide and copper (Cu) accelerates the decomposition process of hydro-peroxides [14].

Oxidized products

Oxidized products in palm oil are peroxides, aldehydes, ketones, and furfurals (from sugars) [8]. These compounds affect palm oil quality at the end of the refining process. They are very difficult to remove during refining. Therefore, palm oil must not be exposed to light, high temperatures, and pro-oxidant compounds.

Minor constituents

Phospholipids are complex esters that consist of nitrogen bases, phosphorus, sugars, and long-chain fatty acids. The existence of phospholipids in the mesocarp of palm oil are about 200 to 1000 ppm and in CPO are about 20 to 80 ppm [14]. These compounds affect the nutrition, stability, and bleaching process of palm oil. There are two types of phospholipids, namely, hydratable and non-hydratable phospholipids. Hydratable phospholipids are easy to remove by using water. These mixtures form liquid crystals. The non-hydratable phospholipids become hydratable phospholipids that are mixed with phosphoric acid or citric acid. Phospholipids are antioxidant-synergistic, and affect pro-oxidants to turn into inactive compounds. Phospholipids are used to remove metal compounds and hydrophilic salt. They decrease the oxidation process in the CPO, too. Phospholipids are removed using phosphoric acid during the degumming process.

Phosphoric acid

There are two types of acidic compounds: phosphoric acid (H_3PO_4) and nitric acid (HNO_3). The (H_3PO_4) is widely used in palm oil refineries in Malaysia since it is easier to administer and cheaper than (HNO_3). The (H_3PO_4) with concentration of 85% is mixed with CPO during the degumming process. Phosphoric acids are odorless and colorless.

Bleaching earth

Bleaching earth can be found in special strata with natural compounds. The role of bleaching earth in the bleaching process is to remove undesired pigment-type compounds in CPO. It is pro-oxidative compound and able to increase the quality of palm oil [15]. Acidic bleaching earth is formed when montmorillonite clay is treated by acidic compounds [16]. Acidic bleaching earth is an excellent metal adsorbent. Its roles are as follows [17]:

- (a) Decrease the existence of chlorophyll and palm oil color.
- (b) Remove phospholipids and soap compounds.
- (c) Decrease free fatty acid compounds in the bleaching process.

Most of these compounds are removed during the refining process. Nurul and Khairiyah [17] have applied Genetic Algorithms (GAs) optimization technique for palm oil refining process. The GA optimizes the dosage of bleaching earth and citric acid in order to improve the quality of the refined oil as well as to increase profit. In 2009, Vintila [18] presented a mathematical model for physical refining whereby a differential vaporization model is applied to simulate the deodorization process in physical refining. However, in this paper, a special type of mathematical modeling, namely graph-based autocatalytic set, is developed for physical palm oil refining process and will be elaborated in the following sections.

4. Graph

Graphs are defined as networks of points or nodes that are connected by links [19]. They are described as a set of lines that connect to a set of points [20].

Definition 1. [19] A directed graph $G = G(V, E)$ is defined by a set of V "vertices" also known as "nodes" and a set E of "edges" or "links" where each edge is an ordered pair of vertices.

All the graphs in Figure 5 are directed graphs. A set of vertices or nodes can be represented as $V = \{v_1, v_2, v_3, \dots, v_n\}$ and $E = \{e_1, e_2, e_3, \dots, e_m\}$ where the vertices and

edges are also known as nodes and links, respectively. The adjacency matrix of a graph is presented as $C = (c_{ij})$. An adjacency matrix is given in the following definition.

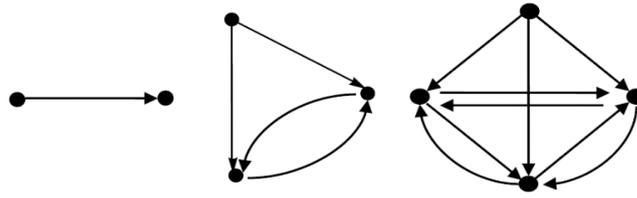


Figure 5. Examples of graphs.

Definition 2. [21] Adjacency matrix of graph $G = G(V, E)$ with n vertices is a $n \times n$ matrix, denoted by, $C = (c_{ij})$ where $c_{ij} = 1$ if E contains a directed link (j, i) (arrow pointing from vertices j to vertices i) and $c_{ij} = 0$ otherwise.

The adjacency matrix of graph G can be described as follows:

$$c_{ij} = \begin{cases} 1 & \text{if } (i, j) \in E \\ 0 & \text{if } (i, j) \notin E \end{cases} \quad (2)$$

and the entries for matrix C_{ij} represent the connection between the i^{th} and j^{th} vertices. Figure 6 shows an example of graph G with four vertices and its adjacency matrix.

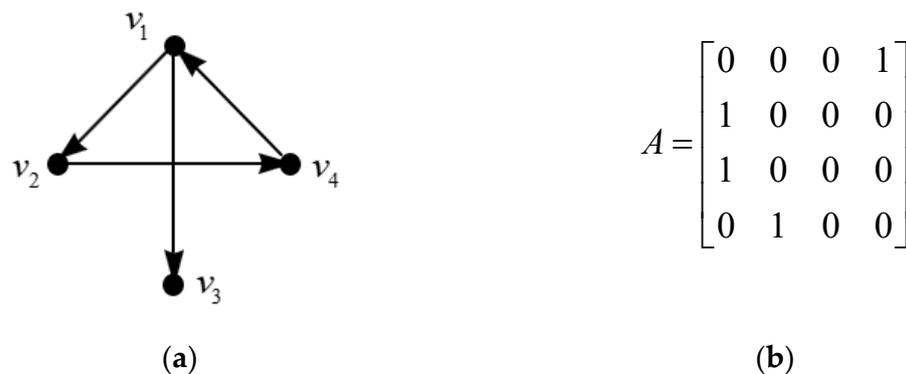


Figure 6. (a) A directed graph; (b) Its adjacency matrix.

The definition of a graph given by Jain and Krishna is slightly different than Definition 1 [22]. The $c_{ij} = 1$ if and only if there is a link from node i to node j . Basically, the resultant adjacency matrix with respect to their definition of a graph is the transpose of the adjacency matrix described by Definition 2.

5. Autocatalytic Set and Dynamicity

A compound used to speed up a chemical reaction is called a catalyst. A catalyst is used to accelerate a slow chemical reaction with the addition of a foreign substance that is not consumed by the reaction itself [23]. In general, an autocatalytic set is defined as a set of entities or a collection of entities where the word entities can be anything such as people, molecules, or objects [24–26]. Jain and Krishna [22] formalized the definition of an autocatalytic set in the form of a graph.

Definition 3. [22] An autocatalytic set is a subgraph, each of whose nodes has at least one incoming link from a node belonging to the same subgraph.

The concept of an autocatalytic set for a graph is defined as vertex j catalyst vertex i [27]. The simplest of ACS graph is a vertex with 1-cycle. Figure 7 illustrates some samples of autocatalytic sets.

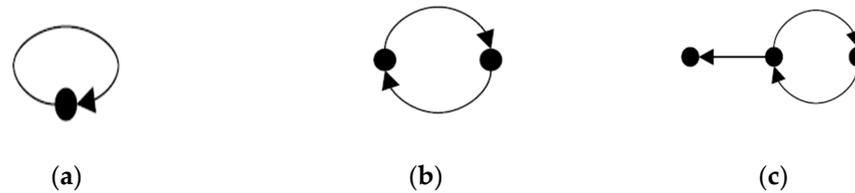


Figure 7. (a) A 1-cycle and ACS; (b) A 2-cycle and ACS; (c) An ACS but not irreducible.

A dynamic system is governed by a set of coupled differential equations, that is given as follows [28–31]:

$$x'_i = \sum_{j=1}^n c_{ij}x_j - x_i \sum_{j,k=1}^n c_{kj}x_j \quad (3)$$

The dynamicity preserves the normalization of x as a state:

$$\sum_{i=1}^n x'_i = 0 \quad (4)$$

Equation (3) plays an important role in system dynamics. It has been used by several researchers such as Eigen et al. [24], who modeled the dynamic of relative populations of a self-replicating string and Jain and Krishna [30,31] applied for catalytically-reacting molecules.

In short, the variable x_i is the i^{th} relative population and designated as $x = \{x_1, x_2, x_3, \dots, x_n\}$. The set x of variables x_i is exactly the set of vertices of the constructed graph such that $i \in \mathbb{N}$. The time evolution of x depends on its interaction coefficients. Each variable x_i has y_i as its concentration. Hence, the relative concentration for each variable is given as follows:

$$x_i \equiv \frac{y_i}{\sum_j y_j} \quad (5)$$

and the sum of for all x_i is as follows:

$$\sum_{i=1}^n x_i = 1 \text{ for } 0 \leq x_i \leq 1 \quad (6)$$

and

$$y'_i = \sum_{j=1}^n c_{ij}y_j - \phi y_i \quad (7)$$

such that $\phi(t)$ is a function at time t . It is a simple idealization of reaction rates in a well-stirred chemical reactor [32].

Sabariah [27] used ACS to model a Clinical Waste Incineration Process. The developed method by the researcher is outlined in the following steps.

Step 1: Construct matrix C with variables x_i evolve through time t using equation (3) as follow:

$$x'_i = \sum_{j=1}^n c_{ij}x_j - x_i \sum_{j,k=1}^n c_{kj}x_j \quad (8)$$

and x_i is large enough to get close to its attractor X , it is donated as $X \equiv x_i(t)$

Step 2: Determine the lowest value of x_i of Perron-Frobenius Eigenvalue (PFE) from the set of vertices $V = \{i \in A | X_i = \min_{j \in A} X_j, A = \{1, 2, 3, \dots, n\}\}$.

The lowest value of x_i is removed from the system along with its edges. Thus, a graph C contains n-1 vertices.

Step 3: Matrix C is reduced to the dimension of $(n - 1) \times (n - 1)$. The remaining vertices and edges of graph C are fixed as they were before. All x_i are updated so that $\sum_{i=1}^{n-1} x_i = 1$ for $0 \leq x_i \leq 1$. The step is repeated until matrix (2×2) is produced.

In Step 1, Equation (3) is introduced to evaluate the dynamical system followed by Step 2 and 3 which describe the procedure to update the graph of the system.

6. Graph of Refining Process of Palm Oil

The graph-based model of physical refining process is elaborated in these subsections.

6.1. Chemical Compounds as Vertices

Firstly, a graphical representation of an ordinary physical refining process is classified as a crisp graph $G_P(V, E)$ whereby V is denoted for the set of vertices and E is the set of edges of the graph G_P that are needed to be determined systematically and properly.

As for refining process of palm oil, the CPO quality depends on the amount of free fatty acids, moisture, heavy metals, oxidized products, and minor constituents in the oil. The unwanted compounds are removed partially or completely during the refining process. The following variables are the vertices for the proposed graph.

6.1.1. Oil

Palm oil consists of free fatty acids (FFA), esterified, and glycerol. Free fatty acids are formed by triglyceride, diglyceride, and monoglyceride. Chemical compounds or enzymatic hydrolysis are used to decompose them.

6.1.2. Moisture

The standard amount of moisture in palm oil varies from 0.15% to 3.0%. It needs to be controlled to prevent FFA from increasing.

6.1.3. Heavy Metals

Heavy metals or trace metals are selected as a vertex in G_P . This particular variable or vertex represents the metal compounds in the refining process. It comprises of iron (Fe), copper (Cu), cadmium (Cd), lead (Pb), and manganese (Mn).

6.1.4. Peroxide

Some oxidized compounds exist in palm oil. They produce odors and unpleasant flavors.

6.1.5. Phospholipids

Phospholipids are complex esters. These compounds consist of nitrogen bases, phosphorus, sugars, and long-chain fatty acids that amount up to 20 to 80 ppm.

6.1.6. Phosphoric Acid

Phosphoric acid (H_3PO_4) is added during the refining process. It is used to remove phosphatide during the degumming process.

6.1.7. Bleaching Earth

Bleaching earth consists of bentonite, attapulgite, and montmorillonite clay. A substantial amount of clay contains iron, magnesium, calcium, silica, and aluminum. Bleaching earth is added during the bleaching process. It is used to remove undesired pigment-type compounds in CPO.

The set of edges, V , of graph G_P is described in the following subsection.

6.2. Chemical Reactions as Edges

The refining process of palm oil consists of seven variables as vertices as described in Section 6 earlier. Figure 8 illustrates the graphical representation of the refining process of palm oil (G_p). The edges are defined as connection such that a vertex catalyzes another vertex.

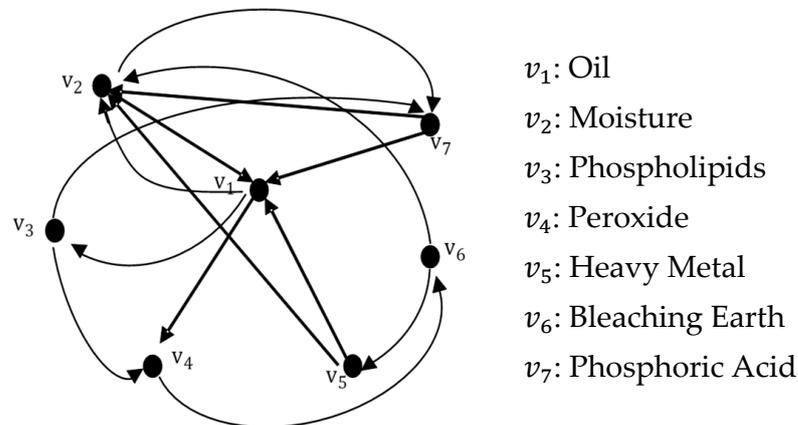


Figure 8. Graph G_p .

For example, (v_1, v_2) represents edge v_1 catalyzes v_2 . The other fourteen edges are chemical reactions described and listed in Table 5.

Table 5. The edges for graph G_p .

Vertices	Edges	Descriptions
(v_1, v_2)	e_1	Oil catalyzes the formation of moisture. The chemical reaction is described formally as follows: $3\text{Fatty acid} + \text{Glycerol} + \text{Zn} \rightarrow \text{Monoglyceride} + \text{H}_2\text{O} + 2\text{Fatty acid}$
(v_1, v_3)	e_2	Phospholipids are produced by chemical reactions of glycerol, adenosine triphosphate (ATP), and glycerol kinase (GK). In other words, oil catalyzes the formation of phospholipids. The balance equation is adopted from [33]. $\text{glycerol kinase (GK)} + \text{Glycerol} + \text{adenosine triphosphate (ATP)} \rightarrow \text{Glycerol-3-phosphate} + \text{ADP}$
(v_1, v_4)	e_3	The CPO is refined at high temperature to produce oxidized compounds. Fatty acid alkyl chains catalyzed the formation of oxidized compounds. $\sim \text{CH} = \text{CH}-\text{CH}_2 \sim + \text{O}_2 \rightarrow \sim \text{CH} = \text{CH}-\text{CH}(\text{OOH}) \sim$
(v_2, v_1)	e_4	Triglycerides oil with moisture is hydrolyzed into free fatty acids and glycerol, i.e., moisture catalyzes oil compounds. $\text{C}_3\text{H}_5(\text{OOCR})_3 + 3\text{HOH} \rightarrow \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{HOOCR}$
(v_2, v_7)	e_5	Moisture catalyzes the formation of H_3PO_4 too. $\text{H}_2\text{PO}_4^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{PO}_4 (\text{aq}) + \text{OH}^- (\text{aq})$
(v_3, v_4)	e_6	Phospholipids such as Glycerol-3-phosphate catalyze the formation of oxidized compounds. The oxidized compound is hydrogen peroxide (H_2O_2). $\text{Glycerol-3-phosphate} \rightarrow \text{H}_2\text{O}_2 + \text{Dihydroxyacetone phosphate} + \text{O}_2 + \text{GPO}$
(v_3, v_7)	e_7	Phospholipase is used as catalyzer for the hydrolysis process that forms ester bonds between the diacylglycerol moiety and phosphoric acid [34].

Table 5. Cont.

Vertices	Edges	Descriptions
(v_4, v_6)	e_8	Bleaching earth consists of silica, aluminum, iron, magnesium, and calcium. When the silicon-carbon bond interacts with peroxide, then silanol (SiOH) is formed [35]. $R-Si + 30\%H_2O_2 \rightarrow ROH + SiOH$
(v_5, v_1)	e_9	Khairil et al. [4] presented his work on esterification process using zinc as a catalyst. Zinc is catalyzed to form oil. $3\text{Fatty acid} + \text{Glycerol} + \text{Zn} \rightarrow \text{Monoglyceride} + \text{H}_2\text{O} + 2\text{Fatty acid}$
(v_5, v_2)	e_{10}	Heavy metals are used as catalyzers in the formation of moisture. This formation is justified by Khairil et al [4].
(v_6, v_2)	e_{11}	Bleaching earth consists of silica, aluminum, iron, magnesium, and calcium. The balance equation below shows that the iron in bleaching earth is catalyzed to form moisture. $H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2H_2O$
(v_6, v_5)	e_{12}	The aluminum in bleaching earth catalyzes the formation of iron. $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$
(v_7, v_1)	e_{13}	Crude glycerol is purified by acidification using phosphoric acid (H_3PO_4) [35]. The H_3PO_4 is catalyzed to form FFA and monopotassium phosphate. Then, H_3PO_4 is catalyzed to form oil. $RCOOK + H_3PO_4 \rightarrow RCOOH + KH_2PO_4$
(v_7, v_2)	e_{14}	The balance equation below shows the production of moisture with weak $H_2PO_4^-$. In other words, H_3PO_4 is catalyzed to form moisture. $OH^- (aq) + H_3PO_4(aq) \leftrightarrow H_2PO_4^- (aq) + H_2O(l)$

7. Dynamicity of G_p

The dynamicity of graph G_p is determined using the procedure described in Section 5. The lowest value for PFE of G_p is discarded; i.e., the chemical compound is depleted. The two surviving chemical compounds are the final products or the outputs of the refining process for palm oil. The quantitative (PFE) and descriptive resultant from the dynamicity of the graph G_p are summarized in Table 6.

Table 6. The dynamic of graph G_p .

Parameter	PFE	Description
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \\ \text{Phospholipids} \\ \text{Peroxide} \\ \text{Heavy Metal} \\ \text{Bleaching Earth} \\ \text{Phosphoric acid} \end{pmatrix}$	$\begin{pmatrix} 0.5163 \\ 0.5754 \\ 0.2506 \\ 0.3722 \\ 0.0877 \\ 0.1806 \\ 0.4009 \end{pmatrix}$	Heavy Metal is depleted
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \\ \text{Phospholipids} \\ \text{Peroxide} \\ \text{Bleaching Earth} \\ \text{Phosphoric acid} \end{pmatrix}$	$\begin{pmatrix} 0.5015 \\ 0.5675 \\ 0.2251 \\ 0.3848 \\ 0.1957 \\ 0.4184 \end{pmatrix}$	Bleaching Earth is depleted

Table 6. Cont.

Parameter	PFE	Description
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \\ \text{Phospholipids} \\ \text{Peroxide} \\ \text{Phosphoric acid} \end{pmatrix}$	$\begin{pmatrix} 0.5196 \\ 0.5196 \\ 0.2825 \\ 0.4361 \\ 0.4361 \end{pmatrix}$	Phospholipids is depleted
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \\ \text{Peroxide} \\ \text{Phosphoric acid} \end{pmatrix}$	$\begin{pmatrix} 0.6015 \\ 0.6015 \\ 0.3717 \\ 0.3717 \end{pmatrix}$	Peroxide is depleted
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \\ \text{Phosphoric acid} \end{pmatrix}$	$\begin{pmatrix} 0.6479 \\ 0.6479 \\ 0.4004 \end{pmatrix}$	Phosphoric acid is depleted
$\begin{pmatrix} \text{Oil} \\ \text{Moisture} \end{pmatrix}$	At the end of the refining process of CPO, oil and moisture are the final products.	

Figure 9 illustrates the updated stages of graph G_p . Initially, it consists of seven vertices, which are reduced to two vertices in the end.

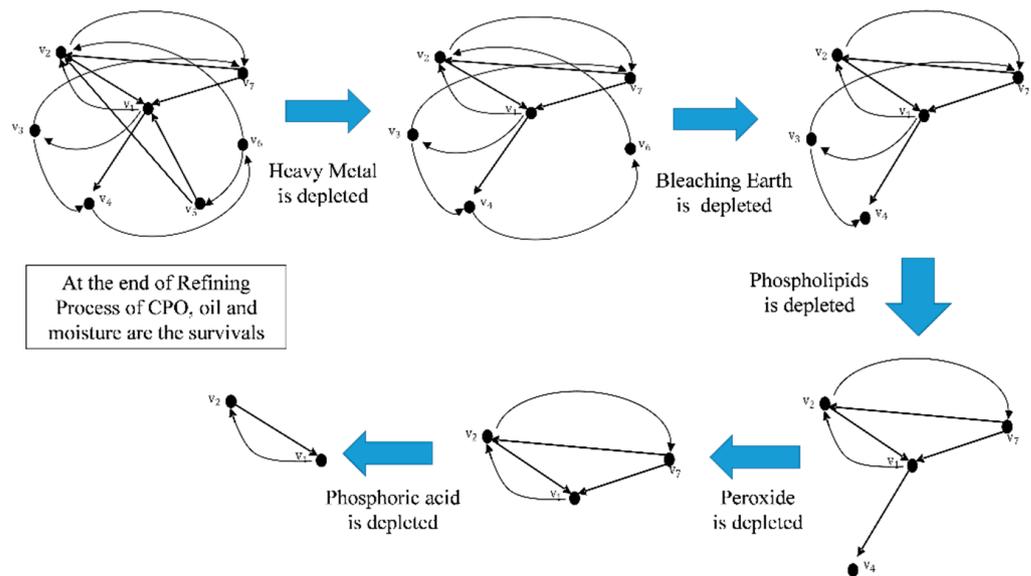


Figure 9. The dynamic of physical refining process of palm oil G_p .

8. Analysis of G_p

The dynamicity of graph G_p is summarized in Table 6 of Section 7 whereby heavy metals are the first variable depleted in the refining process. The sequence of depleted compounds begins with bleaching earth, phospholipids, peroxide, and finally phosphoric acid. The remaining compounds at a given time, t , are summarized as follow (see Table 7):

Table 7. Summary of remaining chemical compounds.

Phase	Chemical Compound
t_0	Oil, Moisture, Phospholipids, Peroxide, Heavy Metal, Bleaching Earth, Phosphoric acid
t_1	Oil, Moisture, Phospholipids, Peroxide, Bleaching Earth, Phosphoric acid
t_2	Oil, Moisture, Phospholipids, Peroxide, Phosphoric acid
t_3	Oil, Moisture, Peroxide, Phosphoric acid
t_4	Oil, Moisture, Phosphoric acid
t_5	Oil, Moisture

Five stages of depleted sequences in the refining process of palm oil are listed above. Further analysis on our obtained rate of change and dynamic of graph G_P are elaborated in Table 8. The results obtained from the proposed method are significantly comparable to results documented in [2,8]. The comparisons are described in the third column of Table 8 (description).

Table 8. Analysis of graph G_P .

Variable	Rate of Change for Graph G_P	Description
Oil Moisture	−2.5076 0.9421	Oil and moisture are determined as survivors at the end of the refining process for palm oil. The negative sign indicates that the amount of oil decreased due to the discarded compounds in the palm oil. Moreover, the palm oil contains more than 2% free fatty acids (FFA). The FFA is removed as palm fatty acid distillate (PFAD). The final product of palm oil from the deodorization process is known as refined bleached deodorized palm oil (RBDPO) [2]. Goh [9] suggested that in order to control the quantity of FFA, CPO should be less than 0.1% of moisture. Even though moisture is present at the end of the refining process, its quantity is smaller than earlier.
Phospholipids	0.8955	Phospholipids are depleted since they contain antioxidant-synergistic characteristics that cause pro-oxidant compounds to become inactive. In general, phospholipids remove metal compounds and hydrophilic salt from the lipid phase and decrease the oxidation in CPO. Phospholipids are removed due to their reactions with phosphoric acid.
Peroxide	0.8956	Peroxide is depleted due to the existence of antioxidants such as phospholipids and heavy metal. The oxidation compounds and carotenoid pigments are removed during the deodorization process in order to preserve the flavor.
Heavy Metal	0.0188	Heavy metals are the first compound depleted since metals are used as catalyzers to decompose hydro peroxides into free radicals. They are also removed during the bleaching process [2].
Bleaching Earth	−0.0546	Bleaching earth is added during the bleaching process. Bleaching earth plays an important role in removing undesired pigment-type compounds in CPO such as phosphoric acid, pigments, trace metals, phosphatides, and oxidation compounds [2]. Therefore, the negative sign is justified as it represents the consumption of bleaching earth when it removes the unwanted compounds.
Phosphoric acid	−0.1899	Similar to bleaching earth, a certain amount of phosphoric acid is added during the refining process. Phosphoric acid is used to remove phospholipids. The negative sign indicates the consumption of these compounds. Finally, the phosphoric acid is consumed by bleaching earth.

Furthermore, the resultant concentrations and dynamicity of graph G_P in this study also concur to results of Er [11], Morad et al. [2], Khairil et al. [5] and Nanda et al. [35]. Moreover, the negativity concentration for some variables from the proposed method are perfectly justified by their role during the refining process.

9. Conclusions

In this paper, the graph-based model for the physical refining process of palm oil is presented. The multidimensional system, namely, the physical refining process for palm oil is defined as graph G_P that consisted of seven vertices and fourteen edges. The concentration rate and dynamicity of graph G_P are evaluated and the results show that oil and moisture are the surviving compounds. The results obtained from the model agreed to the one presented by Er [11] (see Table 8); i.e., these two compounds are the final products

produced by the refining process. The FFA from oil compounds is formed as a palm fatty acid distillate (PFAD). The glycerol and moisture formed refined bleached deodorized palm oil (RBDPO). The PFAD is used as a soap product while RBDPO is utilized as cooking oil. On the other hand, undesired compounds such as phospholipid, peroxide, and heavy metals are removed during the refining process as explained in Table 8.

Author Contributions: Conceptualization, A.A. and T.A.; formal analysis, A.A.; writing—original draft preparation, A.A. and T.A.; writing—review and editing, S.R.A. and N.A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by Ministry of Higher Education Malaysia (MOHE) Fundamental Research Grants FRGS/1/2020/STG06/UTM/01/1 and FRGS/1/2020/STG06/UTM/02/9.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: Authors acknowledge the support of Universiti Teknologi Malaysia (UTM), and Ministry of Higher Education Malaysia (MOHE).

Conflicts of Interest: The authors declare no conflict of interest.

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