# Transesterification of sago starch and waste palm cooking oil in densified $CO_2$

## H Muljana[1], A K Sugih[1], N Christina[1], K Fangdinata[1], J Renaldo[1], Rudy [1], H J Heeres[2], F Picchioni[2]

[1] Department of Chemical Engineering, Parahyangan Catholic University, Ciumbuleuit 94,Bandung 40141, West Java Indonesia
[2] Department of Chemical Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

E-mail : hmuljana@gmail.com

**Abstract.** In this work, the synthesis of biodegradable and yet renewable thermoplastics materials through a transesterification reaction of sago starch and waste palm cooking oil (WPO) in densified $CO_2$ as the solvent is reported. The aim of this research is to investigate the potential used of sago starch and WPO as raw materials in the thermoplastics starch synthesis. The starch esters was successfully synthesized using sago starch and WPO as reagent in densified $CO_2$ as shown from the presence of carbonyl group (C=O, 1743 $cm^{-1}$) in the FT-IR spectra coupled with the presence of the proton ($^1$H-NMR) of the fatty acid in the starch backbone (0.8 – 2 ppm). The product crystallinity decreases as shown in XRD results and resulting with a change in the thermal properties (melting and crystalline temperature) of the products. In addition, the products show a different granular morphology and a higher hydrophobicity compared with native sago starch. This research shows the potential used of sago starch and WPO in the thermoplastics starch synthesis and opens a new perspective on the product application.

## 1. Introduction

Plastics have become indispensable material for daily human activities. This is supported by the fact that number of plastics production increases significantly in the past 20 years, from only about 100 million tons in 1990 and already reach 311 million tons in 2014 [1]. The huge amount of plastics production and their utilization have caused two major problems. The first problem relates with the availability of the raw material. As known, most of plastics are synthesized using precursor derived from the fossil fuel. Approximately 100 million barrels of oil are used to synthesize 8 million tons of plastics [1]. The high demand of fossil fuel for plastics production may cause a problem due to the limited amount of fossil fuel available in the world.

The second problem relates with the high amount of plastics waste in which approximately 50% of the plastic waste ends up in the landfill [1]. This causes serious environmental problem because of high volume to weight ratio and their resistance to degradation [2]. Therefore, the incentive to synthesis a 'green' plastics has significantly arisen in order to overcome the problems described

before. The term 'green' in the plastics synthesis is strongly related with the use of biodegradable materials, renewable feedstocks and safer solvent for the environment [3].

Starch fatty acid ester (FASE) is known as a potential biodegradable thermoplastics material [2]. FASE shows a higher mechanical and thermal properties and has a higher hydrophobicity compared to those of their native counterparts [3,4]. Furthermore, the presence of fatty acid chain in the starch backbone may act as internal plasticizer which beneficial for further processing of the products [4]. FASE is synthesized via esterification of starch with various fatty acid esters such as fatty acid vinyl esters (FAVE) i.e: vinyl laurate,vinyl stearate [3-5], fatty acid methyl esters (FAME) i.e methyl laurate, methyl oleate [6,7] and vegetable oils i.e.: oleic sunflower oil, linseed oil, palm oil [8,9]. In addition, various solvent can be used in the reaction such as DMSO [3,5-6], ionic liquid [7] and densified/supercritical $CO_2$ [4].

The aim of this research is to investigate the potential used of sago starch and waste cooking oil as raw materials in the thermoplastics starch synthesis in densified $CO_2$.  To the best of our knowledge, there is no publication available on the utilization of waste cooking oil in the transesterification of sago starch using densified $CO_2$ as a solvent. Sago starch is used due to its high production in Indonesia (approximately 200.000 tons/year) [10] while its utilization is still limited. In the other hands, waste cooking oil is inexpensive and also abundantly available as waste from food industries, restaurants and many similar facilities [11].  Indonesia was estimated to produce 6.5 million ton of waste cooking oil on 2013 and this is only less than 10% of the worldwide waste cooking oil production [12]. Furthermore, densified $CO_2$ is selected as the solvent not only due to its green properties, but since it can act as a plasticizer for most polymer/biopolymer [13].

This paper deals with a systematic study to evaluate the influence of several process variables such as pressure (15-21 MPa), and catalyst intake ($K_2CO_3$, 0.1 – 0.4 mol/mol anhydroglucose unit (AGU)) on the reactivity as indicated by the Ester Content in the starch ester product (EC). Relevant product properties were determined with Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Contact Angle measurement, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

## 2. Materials and Method

### 2.1 Materials

Sago starch (water content of 16.9 % wt/wt) was purchased from Bina Sago Lestari (Indonesia). Palm Cooking Oil was chosen as the material and was purchased from the local market. The waste palm cooking oil (WPO) was prepared in the laboratory by frying 1 kg of tempeh with 1 kg commercial PO. Prior the experiments, both PO and WPO were analyzed for their fatty acid

composition. The fatty acid composition is comparable with the values reported in literature [14,15]. Analytical grade potassium carbonate ($K_2CO_3$) was purchased from Merck. Technical grade methanol and ethanol was purchased from Bratachem (Indonesia). All chemicals were used as received without further purification. High purity $CO_2$( $\geq$ 98 % volume) and $N_2$ ( $\geq$ 98% volume) were purchased from Sangkuriang (Indonesia).

*2.2    Method*

*2.2.1 Experimental Procedures*

A series of experiments were done by reacting sago starch with waste PO (WPO) at various pressures (15 – 21 MPa), and various $K_2CO_3$ intake (0.1 – 0.4 mol/mol AGU) at a fixed temperature (120 ºC) in densified $CO_2$. Prior the experiment, the free fatty acid (FFA) content of WPO were analyzed according to the procedure published in literature [16]. The FFA contents of WPO was 0.19% wt/wt, suggesting that WPO could directly be used in the experiment without any necessary pretreatment. All the materials (sago starch (2.5 g, dry basis), WPO (3 mol/mol AGU), and $K_2CO_3$ (0.1 – 0.4 mol/mol AGU)) were charged to the autoclave. The starch and WPO intakes were chosen based on the values used in previous experiments [17]. $CO_2$ was introduced inside the reactor using a positive displacement pump equipped with integrated cooling system (Chrom Tech). The reactor was heated to the desired temperature (120 ºC). Additional $CO_2$ was added to increase the pressure to the desired level (depending on the variation, 15 – 21 MPa). After reaction (1.5 h), the reactor was cooled down to room temperature and depressurized. The solid products were filtered to separate from unreacted WPO. The solid products were washed with ethanol (200 mL) and dried in a vacuum oven at temperature of 70 ºC until constant weight.

*2.2.2 Determination of the Ester Content (EC) of the Products*

A hydrolysis method is used to determine the EC values according to a published procedure [8,9]. The following equation was used to calculate the EC values [8,9]:

$$EC = \frac{[(V\,HCl_{\text{blanko}} - VHCl_{\text{sampel}}) \times M\,HCl \times 1000]}{m} \qquad (1)$$

where $V_{NaOH}$ is the volume of NaOH (mL), $V_{HCl}$blanko and $V_{HCl}$ sample are the the titration volume of acid for the blank and fatty acid starch sample (mL) respectively, $M_{HCl}$ molarity of used HCl and m the mass of the fatty acid starch sample (g). $V_{HCl}$ blanko is obtained by the same procedure for native sago starch.

*2.2.3 Analytical Equipment*

Fourier Transform Infrared (FTIR) spectra were performed on a FTIR (IRTracer100 Shimadzu) ATR (attenuated total reflectance) golden gate apparatus (Graseby-Specac Ltd, Orpington, UK). A total 64 scans with a resolution of 4 cm$^{-1}$ were applied.$^{1}$H-NMR spectra were acquired (64 scans, relaxation times of 1.0 s) on an Oxford NMR AS 400 spectrometer operated at 400 MHz using DMSO-d$_6$ as solvent. TGA measurements were performed on a Perkin Elmer TGA 7 Thermogravimetric Analyzer. The samples were heated to 900ºC in an inert atmosphere with a heating rate of 10ºC min$^{-1}$. DSC analyses were performed using a TA Instrument DSC 2920. The sample (about 10 mg) was heated from room temperature to 200ºC (heating rate of 10ºC min$^{-1}$) and was cooled to -50 ºC (cooling rate of 10 ºC min$^{-1}$) and repeated in two cycles [4].

Water contact-angle measurements were performed using an optical contact angle instruments (OCA 15EC, Dataphysics) equipped with SCA software (Dataphysiscs). The morphology were determined using Scanning Electron Microscope on JEOL T330A. X-ray Diffraction (XRD) analyses were done in a diffractometer type PW1710 BASED with Anode Cu. The degree of crystallinity of samples ($X_c$) was quantified as the ratio of the area of the crystalline ($A_c$) reflections and the overall area ($A_t$) following the method of Nara and Komiya (1983) [13,18].

## 3. Results and Discussion

### 3.1  Starch Modification with WPO

A systematic study  were done in order to investigate the effect of pressure and catalyst ratio on the reactivity as shown by the changes in the ester content (EC). Within the experimental range (*vide supra*), a broad Ester Content value is obtained (127.6 – 820.1 meq/kg). The detailed EC obtained in the experiments is shown in Figure 4.

### 3.1.1    Proof of Principle

The FT-IR spectra of native sago starch and starch ester products (EC = 212.6 meq/kg and 820.1 meq/kg)) were acquired and the results are shown in Figure 1. All spectra show several strong absorption bands at 3300 – 3600 cm$^{-1}$ (OH stretching), 2925 – 2950 cm$^{-1}$ (CH stretching), 1609 - 1612 cm$^{-1}$ (OH bending), 1420 cm$^{-1}$ (CH bending), and 900- 1300 cm$^{-1}$ (highly coupled C-O and C-C vibrational modes) [4,7]. These absorption bands are typical bands appeared in FT-IR spectra of starch.

Additional peak at 1743 cm$^{-1}$ is occurred in the spectra of the products corresponds to the presence of carbonyl (C=O) group in the product [4]. This implies the presence of the fatty acid chain in the starch

backbone. The presence of the fatty acid chain also confirmed by the stronger absorption band at 2929 $cm^{-1}$ (CH stretching) compared with the one of native starch as observed in the spectra [4].
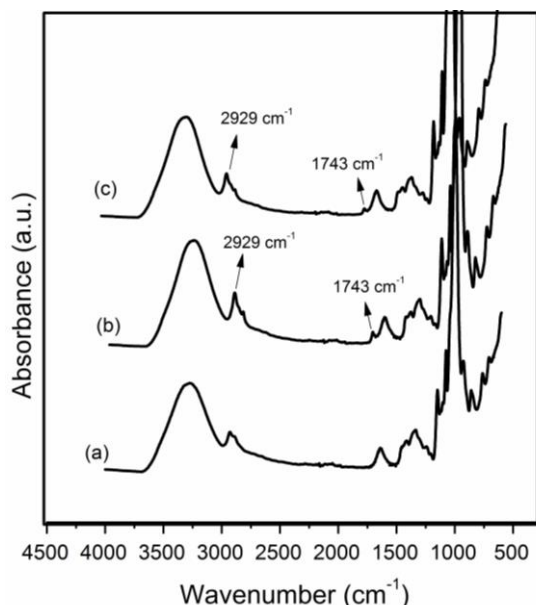


**Figure 1.** FT-IR spectra of native sago starch (a), FASE with EC of 212.6 meq/kg (b) and 820.1 meq/kg (c)

Figure 2 shows the typical $^1$H-NMR spectra of the native starch and the products (EC = 212.6 meq/kg and 820.1 meq/kg). In comparison with the $^1$H-NMR spectra of the native starch, it is clear that all spectra show a broad and overlap peaks in the δ 3.2 to 5.5 ppm range. These peaks are assigned to starch protons [4]. Moreover, additional peaks in the δ 0.8 to 2.5 ppm range are presence in the $^1$H-NMR spectra of the products. These peaks are corresponded to the aliphatic hydrogen atoms of the fatty acid chain. In agreement with FTIR spectra, these observations confirm that the transesterification reaction of sago starch and WPO in densified $CO_2$ was successful.
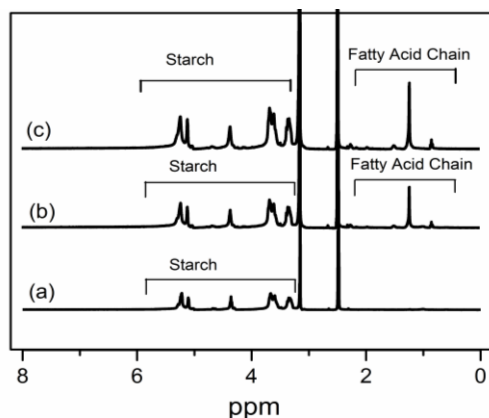


**Figure 2**. $^1$H-NMR spectra of native sago starch (a), FASE with EC of 212.6 meq/kg (b) and 820.1 meq/kg (c)

The change in the morphology of the products is observed using the SEM. The results are shown in Figure 3. The pictures show the change in the granular structure of the products (Figure 3). The native sago starch has an oval granular shape as in agreement with the one reported in literature [19].



(a)                                        (b)                                        (c)
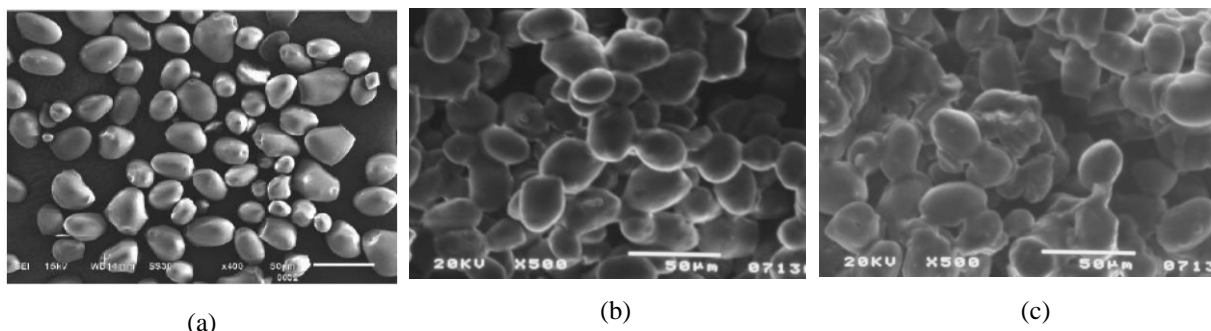
**Figure 3.** SEM pictures of native sago starch (a), FASE with EC of 212.6 meq/kg (b)  and 820.1 meq/kg (c)

The products, in the other hands, show a different granular shape as the native. The granules tend to agglomerate and fuse with each other (Figure 3b and 3c). The similar observation is reported in literature, the agglomeration of the esterified products is possible due to an increase in the hydrogen bond because of the presence of the carbonyl group in the starch backbone [20].

*3.1.2 The Effect of Pressure and $K_2CO_3$ Intake on The Reactivity*

Figure 4 shows the EC values at various pressure and $K_2CO_3$ intake. In all cases, EC reach a maximum values at pressure of 15 MPa and decreases with pressure. The decrease in reactivity with pressure may be related with two competitive effect of pressure on the reaction. The first is plasticizing effect of $CO_2$ on the starch matrices [13]. At higher pressure, more $CO_2$ can be dissolved inside the starch granules, follow by the swelling of the starch matrices and increases the free volume in the starch structure. This leads to a higher diffusion rate of WPO inside the starch granules and increase the reactivity.  In contrary, the second effect, the compressive effect, reduces the free volume of the starch matrices and inhibits the diffusion of the WPO inside the starch granules [4]. The two effects plays important role and influenced the diffusion rate in the reaction and the final EC values.

Similar trend as the pressure effect can also be observed in the effect of $K_2CO_3$ (Figure 4). It is clear that changes in EC values is a strong function of catalyst intake. The trend is somewhat in agreement with our previous result as reported in the literature [21]. This may be related with the possibility that alkaline salt base catalyst ($K_2CO_3$) enhances the hydrolysis reaction of WPO as well and reduce the transesterification reaction rate (lower EC value).  The assumption can be supported by the fact that indeed alkaline base plays role in hydrolysis of triglycerides which is reported as side reaction in the biodiesel production [22].
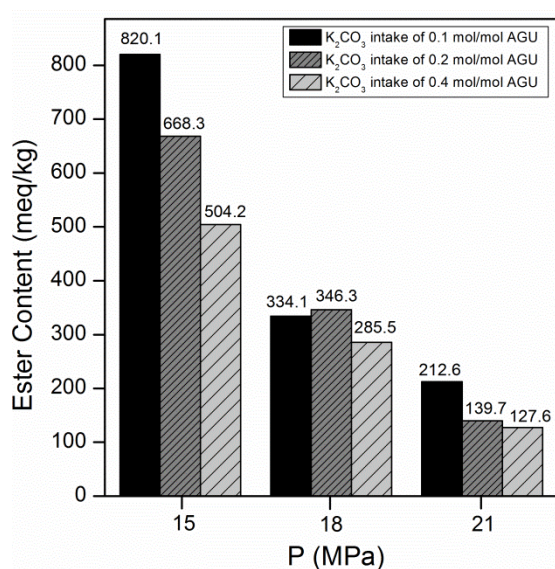
**Figure 4.** Ester Content (EC) values at different pressure and $K_2CO_3$ ratio

## 3.2 Product Characterization

### 3.2.1 X-Ray Diffraction Analysis

The change in the crystallinity of native sago and the products were measured with the XRD analysis. (see Figure 5). It is apparent that all spectra show the characteristics for C-type crystalline patterns of starch with strong diffraction peaks at diffraction angle (2θ) of 15.08º – 15.28º, 17.24 º – 17.3º, 18.04º-18.09 º,  23.12º – 23.18º and 26.7 º – 26.8º [19].
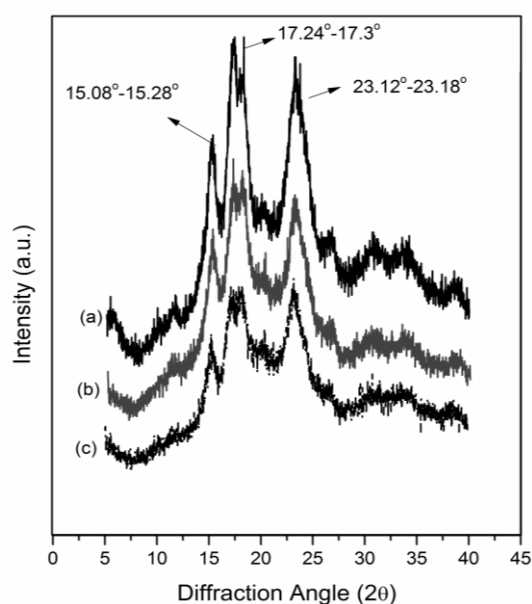


**Figure 5.**  X-Ray Diffractogram of native sago starch (a), FASE with EC of 212.6 meq/kg (b) 820.1 meq/kg (c)

The degree of crystallinity of the native sago and the products is given in Table 1. It is clear that the degree of crystallinity (Xc) decreases at higher Ester Content. This is also confirmed by the result from the DSC measurement (see below). The decrease in crystallinity of the esterified starch products is also reported in our previous work with palm cooking oil (PO) and various fatty acid ester in literature [4], [9]. Within the same range of EC (around 210 meg/kg), FASE synthesized from PO gives the comparable degree of crystallinity (Xc = 0.27) as the one obtained from WPO [9].

The decrease in the crystallinity is happening due to the presence of $CO_2$ in the starch matrices leading to an enhanced plasticizing effect, induces the gelatinization of the starch and eventually reduces the crystallinity of starch [13]. In addition, when starch is gelatinized, the OH group is more susceptible to react with fatty acid chain in the triglycerides. Thus, it is plausible to assume that at higher degree of gelatinization, the degree of crystallinity decreases, starch granules become more reactive and eventually lead to higher EC in the products.

**Table 1.** Degree of crystallinity of native sago and the products

| Sample | Ester Content (meq/kg) | Ac | At | Degree of Crystallinity (Xc) |
|---|---|---|---|---|
| Native Sago |  | 2718.64 | 9624.26 | 0.28 |
| FASE | 212.6 | 1479.95 | 5621.89 | 0.26 |
| FASE | 820.1 | 1767.23 | 7423.85 | 0.24 |

*3.2.2 Thermal Properties of The Products*

Another important feature from the product characterization is their thermal properties. The DSC and TGA results of the native sago and the products are shown in Table 2. Changes in the transition properties of the products compared with the native sago are shown in Table 2.Clearly, the melting enthalpy ($\Delta H_m$) and crystallization enthalpy ($\Delta H_c$) decreases with the EC value. This suggests that the product has a lower crystallinity compared with the one of native starch and the change in crystallinity is a strong function of EC. This is also confirmed by the lower melting temperature ($T_m$) and crystallization temperature ($T_c$) of the products compared with the ones of native starch. Unfortunately, native sago starch displays the transition temperatures ($T_m$ and $T_c$) near or higher than the degradation temperature and therefore cannot be determined accurately. The thermal stability of native sago and the products as obtained from TGA are given in Table 2. It is apparent that both products display a slightly higher thermal stability compared with the native starch [2]. In addition, thermal stability increases at higher EC suggesting that the thermal stability is caused by the presence of fatty acid chain in the starch backbone.

**Table 2.** Thermal Properties and Water Contact Angle results of the native sago and the products

| No | Samples | Ester Content (meq/kg) | Contact Angle | Degradation Temperature Range (ºC) | $T_m$ (ºC) | $\Delta H_m$ (J/g) | $T_c$ (ºC) | $\Delta H_c$ (J/g) |
|----|---------|------------------------|---------------|-------------------------------------|------------|--------------------|------------|--------------------|
| 1 | Native Sago | - | 59.2º | 270 – 275 | | nd* | | |
| 2 | FASE | 212.6 | 88.4º | 278 – 280 | 10.64 | 32.22 | 5.8 | 12.39 |
| 3 | FASE | 400 | 91.1º | nm** | 5.9 | 26.94 | 1.5 | 13.08 |
| 4 | FASE | 820.1 | 89.2º | 282 - 285 | 4.04 | 15.3 | 1.33 | 7.14 |

*nd : not detectable
** nm : not measured

### 3.2.3 Water Contact Angle Measurements

Water contact angle measurements were done on native sago and the products with a range of EC (212.6 – 820.1 meq/kg). For each sample, the measurements were repeated six times to ensure the reproducibility. The contact angle of native sago and the products are shown in Table 2.

In comparison with the native sago starch (59.2º), it is clear that all of the products show a higher contact angle (88.4º – 91.1º). This means that all of the starch products have a higher hydrophobicity compared with native sago starch. The hydrophobicity increases with EC except at EC value of 820.1 meq/kg where small reduction of contact angle is occurred. This can be related to an internal plasticizing effect of fatty acid chain on the starch matrices which expected to increase the starch chain mobility and eventually to a lower surface hydrophobicity [4].

## 4. Conclusions

An exploratory study on the synthesis of fatty acid starch ester with sago starch and waste palm cooking oil (WPO) in densified $CO^2$ is described. The proof of principle is verified by the presence of carbonyl group (C=O, 1743 $cm^{-1}$) in the FT-IR spectra and with the presence of the proton from the fatty acid in the ^{1}H-NMR spectra (0.8 – 2 ppm). The EC of the products is a strong function of pressure and $K_2CO_3$ intake. The morphology, crystallinity, hydrophobicity, and thermal properties of the product are also influenced by the presence of fatty acid chain in the starch backbone and depending on the product EC. The products show a lower crystallinity, higher thermal stability and a higher hydrophobicity compared with native sago starch. This research demonstrates the potential used of sago starch and WPO in the thermoplastics starch synthesis and opens a new perspective on the product application.

**Acknowledgments**

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