University of Groningen

Experimental and modelling studies on the solvent assisted hydraulic pressing of dehulled rubber seeds

Abduh, Muhammad Yusuf; Rasrendra, C. B.; Subroto, Erna; Manurung, Robert; Heeres, Hero J.

Published in:
Industrial Crops and Products

DOI:
[10.1016/j.indcrop.2016.07.025](https://doi.org/10.1016/j.indcrop.2016.07.025)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2016

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Abduh, M. Y., Rasrendra, C. B., Subroto, E., Manurung, R., & Heeres, H. J. (2016). Experimental and modelling studies on the solvent assisted hydraulic pressing of dehulled rubber seeds. *Industrial Crops and Products*, 92, 67-76. <https://doi.org/10.1016/j.indcrop.2016.07.025>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Experimental and modelling studies on the solvent assisted hydraulic pressing of dehulled rubber seeds

Muhammad Yusuf Abduh^{a,b}, C.B. Rasrendra^c, Erna Subroto^a, Robert Manurung^b, Hero J. Heeres^{a,*}

^a Department of Chemical Engineering, ENTEG, University of Groningen, The Netherlands

^b School of Life Sciences and Technology, Institut Teknologi Bandung, Ganesha 10 Bandung, 40132, Indonesia

^c Chemical Engineering Department, Faculty of Industrial Technology, Institut Teknologi Bandung, Ganesha 10 Bandung, 40132, Indonesia

ARTICLE INFO

Article history:

Received 30 December 2015

Received in revised form 21 June 2016

Accepted 19 July 2016

Available online 6 August 2016

Keywords:

Rubber seeds

Hydraulic pressing

Solvent assisted

Regression model

Shirato model

ABSTRACT

A systematic study on the expression of rubber seed oil from dehulled rubber seeds in a hydraulic press was performed in the presence and absence of ethanol. The effect of seed moisture content (0–6 wt%, w.b.), temperature (35–105 °C), pressure (15–25 MPa) and ethanol to seed ratio (0–21%v/w) on the oil recovery was investigated. An optimum oil recovery of 76 wt%, d.b. was obtained (1.6 wt% moisture content, 14%v/w ethanol, 20 MPa, 75 °C, 10 min pressing time). The experimental dataset was modeled using two approaches, viz (i) the Shirato model and (ii) an empirical model using multi-variable non-linear regression. Good agreement between models and experimental data was obtained. Relevant properties of the rubber seed oil obtained at optimum pressing conditions (free fatty acid content, viscosity, density, water and P-content, cold flow properties and flash point) were determined. The pressed rubber seed oil has a relatively low acid value (2.3 mg KOH/g) and is suitable for subsequent biodiesel synthesis.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The rubber tree (*Hevea brasiliensis*) is a perennial plantation crop which has been cultivated mainly as a source of natural rubber. However, the tree also produces a rubber seed, of which the valorisation has received limited attention till now. The yield of rubber seeds is reported to be in the range of 100–1200 kg/ha/yr (Stosis and Kaykay, 1981; Abdullah and Salimon, 2009). From a biorefinery perspective, the identification of high added value outlets for the rubber seeds is highly relevant as it increases the overall value of the value chain from rubber plantation to processed latex (Abduh et al., 2013).

The seeds consist of a kernel surrounded by a hard shell. The kernel contains 40–50% of oil (Ramadhas et al., 2005; Njoku et al., 1996) embedded in a protein rich matrix. The oil, also known as rubber seed oil (RSO), may be a valuable source for biofuel production (Ikwaagwu et al., 2000; Morshed et al., 2011). In addition, it may find applications as lubricants, ingredient in soaps and alkyl resins (Aigbodion and Pillai, 2000). The protein rich matrix may be used as cattle feed, as a feed for biogas production, for binderless

board production (Hidayat et al., 2014) and as a feed for thermochemical processes like pyrolysis (Vaz et al., 2005; Kootstra et al., 2011).

A number of studies have been reported on the expression of RSO from the rubber seeds and these are summarized in Table 1. Most studies involve solvent extraction using a hydrocarbon solvent (hexane, petroleum ether) or a chlorinated solvent. The oil yields cover a wide range and are between 5 and 49%.

Three studies have been performed using mechanical pressing, involving either a hydraulic or screw press. The yields in this case are typically lower than for solvent extraction and between 5.4 and 28.5%. Improved yields are possible by using solvent assisted hydraulic pressing. For instance, Morshed et al. (2011) showed that the use of hexane in mechanical pressing increased the yield from 5.4% to 49% yield (Table 1). Addition of a solvent during oil pressing has also been applied successfully to increase oil yields for the extraction of cotton, sunflower and soybean seeds (Abraham et al., 1993; Dufaure et al., 1999).

Table 1 show that the free fatty acid (FFA) content of the product oils varies from 2 to 38 wt% for the reported studies. For biodiesel synthesis, an FFA value of 3 wt% (Meher et al., 2006) is acceptable. The high FFA values are not necessary an intrinsic feature of the RSO but will depend on the processing conditions and technology,

* Corresponding author at: Department of Chemical Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands.
E-mail address: h.j.heeres@rug.nl (H.J. Heeres).

Table 1
Overview of literature studies on oil isolation from rubber seeds.

Isolation technique	Conditions	Oil Yield ^a	FFA content (wt%) ^c	Reference
Solvent	68–69 °C, <i>n</i> -hexane, 6 h	41.6%	7.6	Abdullah and Salimon (2009)
Solvent	40–60 °C, petroleum ether	45.6%	2	Ikhuagwu et al. (2000)
Solvent	27 °C, carbon tetrachloride, overnight	38.9% ^b	–	Haque et al. (2009)
Solvent	68–69 °C, <i>n</i> -hexane	49%	4	Zhu et al. (2011)
Solvent	68–69 °C, <i>n</i> -hexane, 4 h	45%	–	Ebewele et al. (2010)
Mechanical (hydraulic)	70 °C, 8 MPa, 10 wt% m.c	28.5%	38	Ebewele et al. (2010)
Mechanical	27 °C	5.4%	–	Morshed et al. (2011)
Mechanical + solvent	27 °C, hexane/seed wt. ratio: 0.8%	49%	2	Morshed et al. (2011)

^a Kernel (dehulled seed) unless stated otherwise.

^b Seed estimated from acid value (mg KOH/g).

^c Estimated from acid value (mg KOH/g).

and also by the storage conditions of the seeds (Zhu et al., 2011; Ebewele et al., 2010).

This paper presents a systematic study of the influence of pressure, temperature, moisture content and the use of a solvent on the pressing behaviour of dehulled rubber seeds in a laboratory scale hydraulic press. These process variables have shown to be of high importance for both oil yields and product quality (Venter et al., 2007; Willems et al., 2008; Subroto et al., 2015). A large number of experiments were performed and modeled using appropriate models. Ethanol was selected as the solvent of choice as it may be obtained from renewable resources.

2. Theory: the Shirato model

Several different mathematical models for the expression of oilseeds have been developed, which may be categorised as (i) models based on the nature of cell structures (Mrema and McNulty, 1985), (ii) empirical models (Fasina and Ajibola, 1990), and (iii) Terzaghi-type models (Shirato et al., 1986). The first model type provides fundamental insights in the expression process. However the information of the cell structure and cell dimensions is not easy to obtained, which limits the applicability.

Empirical models enable the prediction of oil yields but are often limited to specific seeds and processing equipment. Terzaghi models allow for a good description of the expression process, however, the model assumes that the cake thickness remains constant during pressing which is often not a good assumption. The Shirato model is a modified Terzaghi-type model. It has been previously applied successfully to model the hydraulic pressing of dry cocoa nibs and several oilseeds (Venter et al., 2007; Willems et al., 2008). It is a dynamic model which uses the cake thickness of a sample as a function of time and processing parameters as input. The cake thickness is expressed as the consolidation ratio (U_c), defined as the difference between cake thicknesses at the start of the process and the cake thickness at time t divide by the maximum difference in cake thickness (before and after the process). This consolidation ratio can be described as a function of time, pressure and material properties (Eq. (1)).

$$U_c(t) = \frac{L(0) - L(t)}{L(0) - L(t_{\text{end}})} = (1 - B) \left\{ 1 - \exp \left(\frac{-\pi^2 C_e t}{4\omega_0^2} \right) \right\} + B \left\{ 1 - \exp \left(- \left(\frac{E}{G} \right) \cdot t \right) \right\}$$

where

$$C_e = \frac{P}{\mu_1 \rho_s \alpha \frac{\partial \varepsilon}{\partial P}} \quad (1)$$

with

U_c consolidation ratio (–)

L_0 cake thickness at t_{initial} (m)

$L(t)$ cake thickness at t_{initial} (m)

L_{end} cake thickness at t_{end} (m)

B relative contribution of secondary consolidation

C_e consolidation coefficient (m^2/s)

ω_0 volume of solids per unit area (m^3/m^2)

t time (s)

E/G creep constant (s^{-1})

P pressure (Pa)

μ_1 liquid viscosity (Pa.s)

ρ_s solids density (kg/m^3)

α filtration resistance (m/kg)

e void ratio (–)

The Shirato model consists of the sum of two terms, primary and secondary consolidation (creep). The relative contribution of the second term is given by the (fit) parameter B . For an individual pressing experiment, the consolidation ratio *versus* time is determined at a constant value of the pressure P . Parameter fitting allows calculation of the value of α , B and E/G for this particular experiment. When performing experiments at different pressures, the values for the individual cake resistances α may be correlated using the following relation:

$$\alpha = \alpha_0 \cdot \left(1 + \frac{P}{P_a} \right)^B \quad (2)$$

where

α_0 material constant for filtration resistance (m/kg)

β material constant for filtration resistance (–)

Parameter fitting for the experiments at different pressures allows calculation of α_0 , the pressure independent filtration resistance and the value of β , which is a measure for the pressure dependence of the cake resistance. A large value for β is indicative for a hard material.

Besides the cake thickness, the oil yield in the form of an oil recovery is also determined for each pressing experiment. The oil recovery can be related to material properties using Eq. (3).

$$\text{Oil recovery (wt\%)} = \left(\frac{(1 - F_0) \varepsilon \rho_o}{(1 - \varepsilon) \rho_s F_0} - 1 \right) \times 100\% \quad (3)$$

With:

ε final average porosity (m^3 non solid/ m^3 total)

F_0 original oil content of the seeds (wt%, d.b.)

ρ_o oil density (kg/m^3)

ρ_s solid density (kg/m^3)

The values for F_0 , ρ_o and ρ_s were determined experimentally in separate experiments (see experimental section for details). In combination with the experimentally determined oil recovery for an individual experiment, the cake porosity ε for each individual experiment may be determined. ε values for experiments at different pressures may be correlated using Eq. (4):

$$(1 - \varepsilon) = (1 - \varepsilon_0) \cdot \left(1 + \frac{P}{P_a} \right)^n \quad (4)$$

Here,

ε_o material constant for porosity (m^3 non solid/ m^3 total)

n material constant for porosity (–)

P_a threshold pressure (Pa)

The threshold pressure was set at 5 MPa.

3. Material and methods

3.1. Material

Seeds from the rubber tree (*Hevea brasiliensis*) were obtained from Bengkulu, Indonesia. Ethanol (absolute, pro analysis) was obtained from Merck (Darmstadt, Germany).

3.2. Moisture content conditioning

The total moisture content of the samples was determined using Method B-1 4 of the German standard methods (DGF, 2002). It involves heating the dehulled rubber seeds in the oven at 103 °C until constant weight.

For experiments at different oil seed moisture contents, the dehulled seeds were heated at 60 °C for a certain time until the desired moisture content was reached. The moisture content of the sample was determined using Method B-1 4. The samples were stored in sealed plastic bags. The moisture content before an actual hydraulic pressing experiment was experimentally determined to ensure that the moisture content was retained and not affected by storage.

3.3. Oil content measurement

The oil content of the rubber seeds used in this investigation was determined using soxhlet extraction, based on method B-1 5 of the German standard methods (DGF, 2002). The seeds were manually dehulled and dried overnight at 103 °C before analysis. The dried kernels were grinded using a coffee grinder. Approximately 5 g of sample was weighed with an accuracy of 0.0001 g and transferred to a soxhlet thimble, covered with cotton wool and extracted with *n*-hexane for at least 6 h. The solvent was evaporated in a rotary evaporator (atmospheric pressure, 69 °C) and the samples were subsequently dried in an oven at 103 °C until constant weight. The oil content is reported as gram oil per gram sample on a dry basis.

3.4. Hydraulic pressing experiments

A schematic representation of the hydraulic press used in this investigation is shown in Fig. 1. The sample was placed on a perforated plate (holes of 1 mm diameter) in the pressing chamber and covered with a stainless steel grid (100 mesh). The temperature in the pressing chamber is adjustable and was between 30 and 120 °C. The pressing chamber was made from stainless steel with a diameter of 20 mm and a height 70 mm. Pressures up to 25 MPa are possible by using a hydraulic plunger. The press is equipped with a thermocouple (± 1 °C) and, a pressure indicator (± 1 MPa), as well as device (Voltcraft VC820) connected to a computer for online monitoring of the cake thickness as a function of time during pressing. Approximately 7 g of sample was placed in the pressing chamber and preheated for 5 min before pressing. The default press setting and the variation of each parameter is shown in Table 2.

In case a solvent was used, the sample was added to the pressing chamber and the appropriate amount of solvent was introduced before the pressure was applied to the sample.

Fig. 1. Schematic representation of the laboratory hydraulic press used in this study (Subroto et al., 2015).

Table 2

Base case and range of variables for hydraulic pressing of dehulled rubber seeds.

Parameter	Base case	Range
Pressure, P (MPa)	20	15–25
Temperature, T (°C)	35	35–105
Moisture content, MC (wt%, w.b.)	2	0–6
Sample weight (g)	7	–
Solvent to seed ratio, SR (% v/w)	0	7–21
Pressing time (min)	10	–

3.5. Design of experiments, statistical analysis and optimization

Non-linear multi-variable regression was used to model the experimental data and for this purpose the Design Expert Version 7.0.0 software package was used. The data were modeled using the following equation:

$$y = b_0 + \sum_{i=1}^4 b_i x_i + \sum_{i=1}^4 b_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 b_{ij} x_{ij} + e \quad (5)$$

Here y is a dependent variable (oil recovery), x_i and x_j are the independent variables (pressure, temperature, moisture content, solvent amount), b_0 , b_i , b_{ii} and b_{ij} are regression coefficients of the model whereas e is the model error.

The regression equations were obtained by backward elimination of non-significant coefficients. A coefficient was considered statistically relevant when the P value was less than 0.05. The optimum conditions for the solvent assisted hydraulic pressing of dehulled rubber seeds were determined using the numerical optimization function provided in the software package.

3.6. Data analyses

Oil yield and oil recoveries were determined for all experiments. The oil yield is defined as the amount of pressed RSO obtained from a certain amount of dehulled rubber seeds (Eq. (6)). The oil recovery is defined as the actual amount of oil obtained from a sample divided by the maximum amount of oil that can be obtained from a certain amount of dehulled rubber seeds, the latter determined

using solvent extraction (Eq. (7)).

$$\text{Yield (wt\%, d.b.)} = \frac{\text{amount of pressed oil (g)}}{\text{intake of rubber seed sample (g)}} \times 100\% \quad (6)$$

$$\text{Oil recovery (wt\%, d.b.)} = \frac{\text{amount of pressed oil (g)}}{\text{oil content by solvent extraction (\%d.b.)} \times \text{intake of rubber seed sample (g)}} \times 100\% \quad (7)$$

All measurements were performed at least in duplicate and the average values are reported.

3.7. Analytical methods

The density of the oils was measured with a picnometer at 10 °C intervals between 30 and 100 °C. For this purpose, 10 ml of a sample was placed in the measuring cell and equilibrated to within 0.1 °C of the desired temperature. Reported values are the average of duplicate measurements.

The viscosity of the sample was determined using a rheometer AR1000-N from TA instrument. A cone-and-plate viscometer was used with a cone diameter of 40 mm and a 2° angle. The measurement was performed at different temperatures with a shear rate of 15 s⁻¹.

The fatty acid composition of the oil was analyzed by gas chromatography–mass spectrometry (GC–MS) using a Hewlett-Packard (HP) 5890 series II Plus device in combination with a with HP chemstation G1701BA using the B0100/NIST library software. Detailed description of the GC method and other analytical methods for water content, acid value, flash point, cloud point and pour point are as described elsewhere (Abduh et al., 2013). The phosphorus content analysis of the RSO was performed at ASG Analytik-Service GmbH, Neuss, Germany according to the method described in EN 14107.

4. Results and discussion

4.1. Rubber seed characteristics

The experiments were carried out using fresh rubber seeds obtained from Bengkulu, Indonesia. The seeds had an average width and length of 2.3–2.5 cm and 2.8–3.0 cm respectively. The seeds consist of a shell (39 wt% d.b.) and a kernel (61 wt% d.b.). Initial moisture content of the seeds and kernels as received were 10 and

8 wt%, w.b., respectively. The dehulled seeds had an average oil content of 49 ± 0.3 wt%, as determined using a standardized Soxhlet extraction with *n*-hexane. This value is at the high end of the oil content range (39–49 wt%) reported in the literature (Table 1).

4.2. Non solvent assisted hydraulic pressing (NSHP)

Exploratory pressing experiments in the absence of a solvent were performed in a laboratory hydraulic pressing machine (Fig. 1) to gain insight on the influence of pressing conditions on the oil recovery of the dehulled rubber seeds. Pressing conditions for the non-solvent hydraulic pressing experiments, particularly the moisture content, temperature and pressure were varied systematically (Table 2). The results of effect of moisture content and temperature are shown in Figs. 2 and 3, respectively. The pressure within the experimental range (15–25 MPa) did not have a significant effect on the oil recovery (63–66 wt%, d.b., figure not shown).

The effect of moisture content on the oil recovery and acid value of the pressed oil are given in Fig. 2. The oil recovery shows an optimum regarding the moisture content and the highest recovery at these non-optimised conditions was about 55 wt% at a moisture content of about 2–3 wt%, w.b. A possible explanation is that at optimum MC values, the pressure is distributed equally in all directions, causing more oil cells to be deformed leading to higher oil release. At higher moisture contents, the liquid phase absorbs most of the pressure load, resulting in a lower oil recovery (Sivala et al., 1991). An overview of optimum moisture contents for the mechanical pressing of various oilseeds is given in Table 3. The values range between 2.1 and 10 wt% for whole and dehulled seeds. Thus, it can be concluded that the optimum moisture content depends on the nature of the oil seeds and the pressing conditions. A higher optimum moisture content was previously reported for dehulled rubber seeds (10 wt%) pressed at 70 °C and 8 MPa (Ebewele et al., 2010). The reported oil yield was 28.5 wt%, d.b., slightly higher than the yield (27.4 wt%, d.b.) obtained in this study.

The moisture content also has a significant impact on the acid value of the product oil, see Fig. 2 for details. The acid value increases from 1.0 to 3.0 mg/kg when going from negligible rubber seed moisture content to 6 wt%, w.b. moisture. At higher moisture contents, the triglycerides are likely more prone to hydrolyses to form free fatty acids (FFA) with a concomitant increase in the acid value.

Thus, it may be concluded that the moisture content is an important process variable that affects both the oil recoveries and the product quality in terms of acidity. Clearly, the use of rubber seeds with low moisture content is favored. The economically optimum moisture content will depend on the balance between process and

Fig. 2. Effect of moisture content of the rubber seeds on oil recovery and acid value of the product oil (20 MPa, 35 °C, solvent free).

Table 3

Optimum moisture content for mechanical pressing of different oilseeds.

Oilseed	Optimum moisture content (wt%)	References
Sesame (whole)	2.1	Willems et al. (2008)
Linseed (whole)	4.7	Willems et al. (2008)
Flax (whole)	2.1	Faborode and Favier (1996)
Cotton (whole)	5.4	Mpagiile and Clarke (2005)
Sunflower (whole)	6	Dedio and Dorrell (1977)
Jatropha (dehulled)	4	Fasina and Ajibola (1990)
Rubber (dehulled)	10	Ebewele et al. (2010)

Fig. 3. Effect of temperature on oil recovery and acid value (20 MPa, 2 wt%, w.b. moisture content, solvent free).

product requirements. Seeds with reduced moisture content will lead to products with a low FFA content and higher oil recoveries, though this goes at the expense of higher cost for seed drying.

The effect of temperature on the oil recovery is given in Fig. 3. The oil recovery increases at higher temperatures (25–110 °C), though seems to level off between 100 and 110 °C. This increase is likely due to temperature induced changes in the physical properties of the dehulled seeds. At elevated temperatures, the dehulled seed tissues are softened and the viscosity of the oil will also be lowered. As a consequence, the permeability increases which enhances the flow of oil through the matrix (Khan and Hanna, 1983; Singh et al., 1984).

Thus, on the basis of the NSHP experiments, the optimum conditions to obtain a reproducible oil recovery of 69 ± 0.4 wt% d.b. and a yield of 34 ± 0.2 wt%, d.b. were at a pressure of 20 MPa, seeds with a moisture content of about 2 wt% and a temperature of 85 °C. The yield is higher compared to other studies reported on the mechanical pressing of rubber seeds (5.4 wt% at 27 °C (Morshed et al., 2011) and 28.5 wt% at 70 °C (Ebewele et al., 2010), see Table 1 for details). This is most probably due to the use of a combination of a higher temperature and lower moisture content in our study.

4.3. Solvent assisted hydraulic pressing experiments (SAHP)

Solvent assisted hydraulic pressing experiments (SAHP) were carried out using ethanol. Ethanol was chosen as a solvent as it is available from renewable resources and poses less handling risks than *n*-hexane (Ferreira-Dias et al., 2003). The ethanol amount to (dehulled) seed was varied between 7 and 21% v/w. The pressure and moisture content were set constant at the optimum conditions obtained in the NSHP experiments except the temperature, which was set at 75 °C (slightly below the boiling point of ethanol).

Fig. 4 shows the effect of solvent to seed ratio on the oil recovery. Addition of ethanol as a solvent has a positive effect on the oil recovery. When using 14%v/w of ethanol on the seeds, the oil recovery increased from 66 in the absence of a solvent to 74 wt%, d.b. in the presence of ethanol. So far, we do not have a sound explanation for the positive effect of ethanol on oil recoveries. It is well possible that the permeability of the oil is enhanced by ethanol assisted rupture of cell structures in the matrix. The effect of the solvent to seed ratio is not very pronounced within the experimental range (7–21%v/w) and this is confirmed by subsequent experiments and modeling activities (*vide infra*). A previous study on solvent-assisted extru-

Fig. 4. Effect of solvent to seed ratio on oil recovery (20 MPa, 75 °C, 2 wt%, w.b. moisture content).

sion of sunflower seeds showed an increase of 6 wt% in oil recovery when 2-ethylhexanol was used as a solvent (Dufaure et al., 1999), close to the value found in this study (8 wt% improvement). Based on these findings, a 14%v/w ratio of ethanol on dehulled seeds was selected as the base case for subsequent modeling studies.

4.4. Data modeling using the Shirato model for NSHP and SAHP

4.4.1. Estimation of material properties

The Shirato model was applied to model the experimentally determined cake heights in the form of a consolidation ratio versus the time. In combination with the experimentally determined oil recoveries, it also allows determination of among others relevant material properties of dehulled rubber seeds. A total of 20 experiments were performed in a range of pressing conditions and the results are shown in Fig. 5 and Tables 4–5.

The Shirato model gives a good description of the SAHP and NSHP of rubber seeds, see Fig. 5 for details. The values for *B*, a measure for secondary consolidation (creep) is between 0.04 and 0.17, indicating that primary consolidation is by far more important. The creep constant *E/G* varies between 0.056 and 0.092. The experimental data obtained isothermally at different pressures (exp. 9–17 in Table 4) allows calculation of the values for ϵ_0 , *n*, α_0 , β (section 2.3 for more details). These are given in Table 5 for both SAHP and NSHP and will be discussed in the following.

The values for *B* for SAHP and NSHP are equal and indicate that the contribution of secondary consolidation to the total process for both SAHP and NSHP is comparable. The same holds for the creep constant (*E/G*), indicating that secondary consolidation is not influenced by the presence of ethanol. However, the material constants like porosity and filtration resistance differ considerably for SAHP and NSHP, see Table 5 for details. Dehulled rubber seeds forms a very dense cake at all pressures investigated leading to relatively high filtration resistances (high value of α_0). The calculated α_0 for the NSHP model is in the same order of magnitude as those reported for cellular biological solids (Schwartzberg, 1997). The value of α_0 for SAHP of rubber seed kernels is one order of magnitude lower than in the absence of a solvent. Possibly, the addition of ethanol increases the permeability of oil and rupture of cell structures in the matrix (Gandhi et al., 2003). The addition of solvent also reduced the pressure dependency of the filtration resistance as shown by lower value of β for SAHP in comparison with NSHP.

Table 4Overview of experiments for dehulled rubber seeds at different pressing conditions.^a

No.	T (°C)	MC (wt%, w.b.)	SR (%v/w)	P (MPa)	B ^b (–)	E/G ^b (–)	α^b (m/kg)
1	35	0	–	20	0.04	0.0056	3.8×10^{11}
2	35	2	–	20	0.07	0.0068	3.6×10^{11}
3	35	4	–	20	0.09	0.0056	4.1×10^{11}
4	35	6	–	20	0.10	0.0051	3.9×10^{11}
5	65	2	–	20	0.10	0.0055	3.5×10^{11}
6	85	2	–	20	0.14	0.0057	3.6×10^{11}
7	105	2	–	20	0.17	0.0092	3.8×10^{11}
8	75	2	–	15	0.08	0.0056	2.5×10^{11}
9	75	2	–	20	0.07	0.0051	3.4×10^{11}
10	75	2	–	25	0.16	0.0075	4.0×10^{11}
11	65	2	14	15	0.09	0.0066	2.2×10^{10}
12	65	2	14	20	0.11	0.0066	2.6×10^{10}
13	65	2	14	25	0.12	0.0061	3.4×10^{10}
14	75	2	14	15	0.12	0.006	3.6×10^{10}
15	75	2	14	20	0.09	0.0052	6.6×10^{10}
16	75	2	14	25	0.12	0.0061	9.7×10^{10}
17	55	2	14	20	0.12	0.0069	1.8×10^{10}
18	75	2	14	20	0.1	0.006	6.4×10^{10}
19	65	2	7	20	0.12	0.0069	2.3×10^{10}
20	65	2	21	20	0.09	0.0074	2.5×10^{10}

^a T: temperature, MC: moisture content, SR: solvent to seed ratio, P: pressure.^b Obtained by parameter fitting using Eq. (1).**Table 5**

Material properties estimated from the Shirato model.

Parameter	Dehulled rubber seed ^a	Dehulled rubber seed ^b	Dehulled rubber seed ^c	Dehulled Jatropha seed ^d	Whole linseed ^e
ε_0 (–)	0.67 ± 0.004	0.66 ± 0.002	0.67 ± 0.003	0.32	0.56
n (–)	0.02 ± 0.007	0.02 ± 0.001	0.04 ± 0.002	0.09	0.19
R ²	0.93	0.96	0.96	0.99	0.97
α_0 (m/kg)	9.5×10^{10}	9.9×10^{10}	6.7×10^{11}	6.8×10^{10}	3.7×10^9
B	1.08 ± 0.1	1.16 ± 0.12	1.44 ± 0.02	0.48	1.55
R ²	0.97	0.97	0.97	0.63	0.99
B (–)	0.11 ± 0.02	0.11 ± 0.02	0.11 ± 0.06	0.64 ± 0.08	0.12 ± 0.06
E/G (s ^{–1})	0.006 ± 0.0003	0.006 ± 0.0004	0.006 ± 0.001	0.005–0.006	0.006–0.008

^a 65 °C, 15–25 MPa, 2 wt%, w.b., 14% v/w of solvent.^b 75 °C, 15–25 MPa, 2 wt%, w.b., 14% v/w of solvent.^c 75 °C, 15–25 MPa, 2 wt% w.b., solvent free.^d 40 °C, 20–70 MPa, dry seeds, solvent free (Willems et al., 2008).^e 40 °C, 10–70 MPa, dry seeds, solvent free (Willems et al., 2008).

From Table 5, it can be observed that dehulled rubber seeds have a lower value of n (0.02–0.04) as compared to dehulled jatropha (0.09) and whole linseed (0.19). This indicates that the pressure dependency of the porosity is relatively limited (Willems et al., 2008). A lower value of n implies that dehulled rubber seed is less compressible as compared to dehulled jatropha at the studied conditions. Addition of a solvent slightly decreased the porosity and its pressure dependence. The relatively high values of β in comparison to dehulled jatropha seed (0.48) indicate that dehulled rubber seeds can be considered to be highly compressible material at the conditions studied (Willems et al., 2008).

4.4.2. Effect of operating conditions on consolidation ratio for NSHP

From preliminary NSHP screening experiments (*vide supra*), the temperature and moisture content were shown to have the largest effects on oil recoveries compared to pressure and solvent to seed ratio (Figs. 2–4). As such, these variables were studied in more detail by performing additional experiments (Table 4) for NSHP and the results were modeled using the Shirato model. The experimental ranges were between 0 and 6 wt% for the moisture content and 35–105 °C for the temperature (Table 2).

The effect of moisture content on the consolidation ratio *versus* time is given in Fig. 6. The final consolidation ratio is essentially similar for all MC's but the final value is achieved at a shorter time for lower moisture contents. The contribution of secondary consolidation increases with an increase in moisture content as

illustrated in Fig. 7. The creep constant and specific filtration resistance are approximately independent of the moisture content (see Fig. 1, Supplementary data). These trends are in agreement with the results reported for the hydraulic pressing of sesame seed (Willems et al., 2008).

The effect of the temperature on the consolidation ratio *versus* time is given in Fig. 7. Higher temperatures in the range 35–85 °C results in a more rapid decrease in the filter cake thickness. These findings may be explained by considering that the elasticity of the solid matrix increases at higher temperatures and becomes highly compressible (Venter et al., 2007; Willems et al., 2008; Subroto et al., 2015). However, a further increase from 85 to 105 °C does not lead to an increase in the rate of expression. Thus, on the basis of the experimental data and supported by the Shirato model, we can conclude that the rate of expression for NSHP increases with (i) pressing temperature till a maximum at 85 °C and (ii) when using rubber seeds with a low moisture content.

4.5. Empirical modeling of oil recoveries using design of experiments for SAHP

To gain further detailed insights in the effects of process variables on oil recovery for SAHP, a new set of experiments was performed and the data were modeled using multi-variable non-linear regression. The pressing conditions and particularly the moisture content, temperature, pressure and solvent to seed ratio were varied systematically using a four-factor face centered Cen-

Fig. 5. Consolidation ratio versus time and parity plot for typical SAHP and NSHP experiments using dehulled rubber seeds (SAHP: 20 MPa, 75 °C, 2 wt%, w.b. moisture content, 14%v/w, NSHP: 20 MPa, 75 °C, 2 wt%, w.b. moisture content, solvent free).

Table 6

Level and range of variables for the CCD for SAHP.

Factors	Levels		
	−1	0	1
Pressure, P (MPa)	15	20	25
Temperature, T (°C)	55	65	75
Moisture content, MC (wt%, w.b.)	1	2	3
Solvent to seed ratio, SR (%v/w)	7	14	21

tral Composite Design (CCD, Table 6) and a total of 30 experiments was performed.

The experimental oil recoveries were between 53.3–73.8 wt%, d.b (Table 7), indicating that the pressing variables have a large impact on the oil recovery. The effect of pressing conditions on the oil recovery was modeled and the model coefficients are given in Table 8. The ANOVA data are provided in Table 9 and reveal that the model describes the experimental data very well (low p -value, high R -squared values). This is also illustrated by a parity plot showing the experimental and modeled oil recovery (Fig. 8). The solvent to seed ratio (SA) was not statistically relevant ($p > 0.05$) and was

Fig. 6. Consolidation ratio versus time at different moisture contents (35 °C, 20 MPa, solvent free).

Fig. 7. Consolidation ratio versus time at different temperatures (20 MPa, 2 wt%, w.b., solvent free).

excluded from the model. A visualisation of the effect of process variables on the oil recovery is given in Fig. 9. Higher temperatures have a positive effect on the oil recovery. An optimum in oil recovery for both moisture content and pressure was observed, the exact value being a function of the other process variables.

The Design Expert software allows calculation of the optimum conditions to attain the highest oil recovery for the SAHP in the experimental window. A number of optima (5) with oil recoveries of about 75% were calculated, all at a pressure of 20 MPa, a temperature of 75 °C, and a moisture content between 1.3 and 1.9 wt%. An experiment was performed at one of these optima (moisture content 1.6 wt%, solvent to seed ratio of 14%v/w) to verify the model predictions. Good agreement between experimental (75.7%) and modeled oil recovery (75.4%) was observed.

4.6. Composition and relevant product properties of RSO

The fatty acid composition of the pressed oil obtained at optimum pressing conditions for SAHP (20 MPa, 1.6 wt%, w.b., 75 °C,

Table 7
Experimental conditions and the percentage of oil recovery (wt%, d.b.).^a

No	P (MPa)	T (°C)	MC (wt%, w.b.)	SR (% v/w)	Oil recovery (wt%, d.b.)	
					Actual	Predicted
1	25	55	3	7	54.7	53.7
2	25	65	2	14	69.0	69.1
3	15	65	2	14	67.5	68.2
4	15	75	3	7	58.9	57.1
5	15	55	3	21	55.4	52.7
6	15	75	3	21	56.3	57.1
7	15	55	3	7	50.0	52.7
8	15	75	1	21	70.9	71.4
9	25	55	1	7	64.7	63.9
10	20	65	2	7	68.7	70.5
11	25	55	3	21	53.3	53.7
12	15	55	1	21	64.6	62.9
13	20	65	2	21	72.6	70.5
14	25	75	3	7	57.5	58.1
15	25	75	3	21	57.9	58.1
16	20	65	2	14	71.0	70.5
17	25	75	1	7	72.8	72.3
18	20	65	2	14	73.0	70.5
19	20	65	2	14	69.0	70.5
20	20	65	2	14	69.0	70.5
21	20	65	2	14	70.0	70.5
22	20	65	3	14	56.4	57.2
23	20	65	1	14	69.5	69.5
24	15	75	1	7	70.4	71.4
25	15	55	1	7	62.4	62.9
26	25	55	1	21	62.0	63.9
27	25	75	1	21	73.2	72.3
28	20	65	2	14	72.0	70.5
29	20	75	2	14	73.8	73.7
30	20	55	2	14	66.9	67.3

^a P: pressure, T: temperature, MC: moisture content, SR: solvent to seed ratio.

Table 8
Coefficients for the empirical model of oil recovery for SAHP (wt%, d.b.).

Variable	Coefficient
Constant	−11.61
P	3.06
T	0.53
MC	29.1
T.MC	−0.1
P ²	−0.074
MC ²	−7.15

P: pressure (MPa), T: temperature (°C), MC: moisture content (wt%, w.b.).

Table 9
Analysis of variance for the SAHP of dehulled rubber seeds.

	SS	DF	MS	F	p-value	R ² values
Model	1410	6	235	104	<0.0001	R ²
Error	52	23	4.7			R ² _{adjusted}
Total	1462	29				R ² _{predicted}

14%v/w) was determined (GC) and shown to consist mainly of palmitic acid (12.2%), stearic acid (7.3%), oleic acid (28.1%), linoleic acid (38.2%) and linolenic acid (14.2%). The measured fatty acid composition is in the same range as reported by [Ramadhas et al. \(2005\)](#) viz.; 10.2% palmitic acid, 8.7% stearic acid, 24.6% oleic acid, 39.6% linoleic acid and 16.3% linolenic acid.

Relevant product properties of the pressed RSO after quantitative ethanol removal (GC) are shown in [Table 10](#). The acid value of the oil is (2.3) relatively low compared the acid value reported for RSO in the literature (2–38 mg KOH/g, [Table 1](#)). A possible explanation for the low value is that the seeds used in this study were freshly obtained from the plantation and directly dried to a MC below 7 wt% before storage ([Ebewele et al., 2010](#)). The flash point (290 °C) is within the range as reported in the literature

Fig. 8. Parity plot for the empirical model for SAHP.

Fig. 9. Response surface showing the interaction between two parameters on oil recovery (a) temperature and pressure (2 wt%, w.b., 14%v/w) (b) moisture content and temperature (20 MPa, 14%v/w).

Table 10
Properties of pressed RSO at optimum conditions (20 MPa, 1.6 wt%, w.b., 75 °C, 14%v/w ethanol/seed ratio).

Property	RSO
Acid value (mg KOH/g)	2.3
Water content (mg/kg)	300
P content (mg/kg)	57.7
Flash point (°C)	290
Pour point (°C)	−4
Cloud point (°C)	0

Fig. 10. Cold flow properties of RSO and other plant oils.

(198–294 °C) (Ramadhas et al., 2005; Njoku et al., 1996), as well as the cloud point (0 °C versus –1–0 °C in literature). Data for the pour point of RSO are not available in the literature. The pour point for RSO is close to the reported value for RSO methyl ester (–5 to –8 °C) (Ramadhas et al., 2005; Njoku et al., 1996). The cloud point and pour point of RSO in comparison to palm oil (Crabbe et al., 2001), ground nut oil (Gunstone et al., 2007) and rapeseed oil (Balat, 2007) are presented in Fig. 10. The pour point, which is a function of the degree of unsaturation of the fatty acid chains and typically decreases with higher unsaturation level, is in the expected range for plant oils (Ming et al., 2005).

The P content (58 ppm) is higher than the threshold limit (3 mg/kg) set by the pure plant oil quality standard DIN 51605 (www.eia.gov, 2014). For biodiesel synthesis, a phosphorous content above 50 ppm may reduce the yield by 3–5% (Van Gerpen, 2005). Thus, a purification and particularly a degumming procedure will be required before the RSO can be used for efficient biodiesel synthesis.

The temperature dependence of the density and viscosity of the pressed rubber seed oil are required input for the Shirato model (Eq. (1)). Both properties were measured at a range of temperatures (see Fig. 2 Supplementary data) and fitted using Eqs. (8) and (9):

$$\rho = \rho_1 - \rho_0 T \quad (8)$$

$$\mu = \mu_0 \exp(-\mu_1/(RT)) \quad (9)$$

Good fits were obtained (R^2 of 0.99) with values for ρ_0 and ρ_1 of $6.94 \times 10^{-4} \text{ g}/(\text{cm}^3 \cdot ^\circ\text{C})$ and $0.948 \text{ g}/\text{cm}^3$, respectively and μ_0 and μ_1 values of $4.59 \times 10^{-6} \text{ Pa}\cdot\text{s}$ and $23.1 \times 10^3 \text{ J}/\text{mol}$, respectively.

5. Conclusions and outlook

Systematic experiments on rubber seed oil expression have been performed both in the absence (NSHP) and presence of ethanol (SAHP). In the absence of a solvent (NSHP), the highest oil recoveries (69 wt%) were obtained at 2 wt% moisture content, 20 MPa, 85 °C and 10 min pressing time. A 7% improvement in oil recovery was possible by expression in the presence of ethanol (SAHP) at 1.6 wt% moisture content, 14%v/w ethanol, 20 MPa, 75 °C and 10 min pressing time.

The experimental dataset was modeled using two approaches, viz. (i) a fundamental dynamic model known as the Shirato model for the consolidation ratio versus the time profiles (NSHP and SAHP) and (ii) an empirical model for oil recoveries using multi-variable non-linear regression (for SAHP). Both models gave a good descrip-

tion of the experimental data. Parameter estimation for the Shirato model indicates that the dehulled rubber seeds are relatively hard materials as indicated by the low value of n (0.02–0.04) as compared to dehulled jatropha seeds (0.09) and whole linseed (0.19). In addition, we can conclude that the rate of expression for NSHP increases with (i) pressing temperature till a maximum at 85 °C and (ii) when using rubber seeds with a low moisture content. The non-linear regression model for the oil recovery using SAHP suggests that the moisture content of the dehulled seeds and temperature have the largest effect on the oil recovery followed by pressure and solvent to seed ratio. At optimum conditions, a reproducible oil recovery of 76 and an oil yield of 37 wt%, d.b. were obtained.

Relevant properties of the RSO were determined and indicate that the RSO obtained in this study can be used as a feedstock for biodiesel production, provided that the P content is reduced e.g. by degumming. The use of SAHP with ethanol may have advantages when aiming for the production of fatty acid ethyl esters (FAEE). Integration of an initial SAHP of the seeds followed by subsequent ethanolysis of the RSO produced is an attractive process option as it (i) leads to higher overall biodiesel yields due to improved RSO recoveries in the first step when using ethanol assisted oil expression and (ii) eliminates the use of ethanol separation from the RSO after the oil expression by e.g. distillation, which is energy and capital intensive.

Acknowledgement

The authors thank NWO/WOTRO for a research grant in the framework of the Agriculture beyond Food program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.indcrop.2016.07.025>.

References

- Abduh, M.Y., Van Ulden, W., Kalpoe, V., Van de Bovenkamp, H.H., Manurung, R., Heeres, H.J., 2013. Biodiesel synthesis from *Jatropha curcas* L. oil and ethanol in a continuous centrifugal contactor separator. *Eur. J. Lipid Sci. Technol.* 115, 123–131.
- Abdullah, B., Salimon, J., 2009. Physicochemical characteristics of Malaysian rubber (*Hevea Brasiliensis*) seed oil. *Eur. J. Sci. Res.* 31, 437–445.
- Abraham, G., Sr, R.H., Kuk, M., Wan, P., 1993. Water accumulation in the alcohol extraction of cottonseed. *J. Am. Oil Chem. Soc.* 70, 207–208.
- Aigbodion, A., Pillai, C., 2000. Preparation, analysis and applications of rubber seed oil and its derivatives in surface coatings. *Prog. Org. Coat.* 38, 187–192.
- Balat, M., 2007. Production of biodiesel from vegetable oils: a survey. *Energy Sources Part A* 29, 895–913.
- Crabbe, E., Nolasco-Hipolito, C., Kobayashi, G., Sonomoto, K., Ishizaki, A., 2001. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. *Process Biochem.* 37, 65–71.
- Dedio, W., Dorrell, D., 1977. Factors affecting the pressure extraction of oil from flaxseed. *J. Am. Oil Chem. Soc.* 54, 313–315.
- Dufaure, C., Mouloungui, Z., Rigal, L., 1999. A twin-screw extruder for oil extraction: II. Alcohol extraction of oleic sunflower seeds. *J. Am. Oil Chem. Soc.* 76, 1081–1086.
- Ebewele, R., Iyayi, A., Hymore, F., 2010. Considerations of the extraction process and potential technical applications of Nigerian rubber seed oil. *Int. J. Phys. Sci.* 5, 826–831.
- Faborode, M., Favier, J., 1996. Identification and significance of the oil-point in seed-oil expression. *J. Agric. Eng. Res.* 65, 335–345.
- Fasina, O., Ajibola, O., 1990. Development of equations for the yield of oil expressed from conophor nut. *J. Agric. Eng. Res.* 46, 45–53.
- Ferreira-Dias, S., Valente, D.G., Abreu, J.M., 2003. Comparison between ethanol and hexane for oil extraction from *Quercus suber* L. fruits. *Grasas Aceites* 54, 378–383.
- Gandhi, A., Joshi, K., Jha, K., Parihar, V., Srivastav, D., Raghunadh, P., Kawalkar, J., Jain, S., Tripathi, R., 2003. Studies on alternative solvents for the extraction of oil-I soybean. *Int. J. Food Sci. Technol.* 38, 369–375.
- Gunstone, F.D., Hardwood, J.L., Dijkstra, A.J., 2007. *The Lipid Handbook*. CRC Press, Boca Raton.

- Haque, M., Islam, M., Hussain, M., Khan, F., 2009. Physical, mechanical properties and oil content of selected indigenous seeds available for biodiesel production in Bangladesh. *CIGR J.* 11.
- Hidayat, H., Keijsers, E., Prijanto, U., Van Dam, J., Heeres, H.J., 2014. Preparation and properties of binderless boards from *Jatropha curcas* L. seed cake. *Ind. Crops Prod.* 52, 245–254.
- Ikwuagwu, O., Ononogbu, I., Njoku, O., 2000. Production of biodiesel using rubber *Hevea brasiliensis* (Kunth Muell.) seed oil. *Ind. Crops Prod.* 12, 57–62.
- Khan, L., Hanna, M., 1983. Expression of oil from oilseeds—a review. *J. Agric. Eng. Res.* 28, 495–503.
- Kootstra, A.M.J., Beftink, H.H., Sanders, J.P., 2011. Valorisation of *Jatropha curcas*: solubilisation of proteins and sugars from the NaOH extracted de-oiled press cake. *Ind. Crops Prod.* 34, 972–978.
- Meher, L., Sagar, D.V., Naik, S., 2006. Technical aspects of biodiesel production by transesterification—a review. *Renew. Sustain. Energy Rev.* 10, 248–268.
- Ming, T.C., Ramli, N., Lye, O.T., Said, M., Kasim, Z., 2005. Strategies for decreasing the pour point and cloud point of palm oil products. *Eur. J. Lipid Sci. Technol.* 107, 505–512.
- Morshed, M., Ferdous, K., Khan, M.R., Mazumder, M., Islam, M., Uddin, M.T., 2011. Rubber seed oil as a potential source for biodiesel production in Bangladesh. *Fuel* 90, 2981–2986.
- Mpagalile, J.J., Clarke, B., 2005. Effect of processing parameters on coconut oil expression efficiencies. *Int. J. Food Sci. Nutr.* 56, 125–132.
- Mrema, G., McNulty, P., 1985. Mathematical model of mechanical oil expression from oilseeds. *J. Agric. Eng. Res.* 31, 361–370.
- Njoku, O., Ononogbu, I., Owusu, A., 1996. An investigation on oil of rubber seed (*Hevea brasiliensis*). *J. Rubber Res. Inst. Sri Lanka* 78, 52–59.
- Ramadhas, A.S., Jayaraj, S., Muraleedharan, C., 2005. Biodiesel production from high FFA rubber seed oil. *Fuel* 84, 335–340.
- Schwartzberg, H.G., 1997. Expression of fluid from biological solids. *Sep. Purif. Methods* 26, 1–213.
- Shirato, M., Murase, T., Iwata, M., Nakatsuka, S., 1986. The Terzaghi-Voigt combined model for constant-pressure consolidation of filter cakes and homogeneous semi-solid materials. *Chem. Eng. Sci.* 41, 3213–3218.
- Singh, M., Farsaie, A., Stewart, L., Douglass, L., 1984. Development of mathematical models to predict sunflower oil expression. *J. Am. Oil Chem. Soc.* 79, 165–170.
- Sivala, K., Bhole, N., Mukherjee, R., 1991. Effect of moisture on rice bran oil expression. *J. Agric. Eng. Res.* 50, 81–91.
- Stosic, D., Kaykay, J., 1981. Rubber seeds as animal feed in Liberia. *World Anim. Rev.* 39, 29–39.
- Subroto, E., Manurung, R., Heeres, H.J., Broekhuis, A.A., 2015. Mechanical extraction of oil from *Jatropha curcas* L. kernel: effect of processing parameters. *Ind. Crops Prod.* 63, 303–310.
- Van Gerpen, J.H., 2005. Biodiesel processing and production. *Fuel Process. Technol.* 86, 1097–1107.
- Vaz, C.M., de Graaf, L.A., Mulder, W.J., 2005. Adhesives, Coatings, and Bioplastics from Protein Sources. *Biopolymers Online* 8.
- Venter, M., Kuipers, N., De Haan, A., 2007. Modelling and experimental evaluation of high-pressure expression of cocoa nibs. *J. Food Eng.* 80, 1157–1170.
- Willems, P., Kuipers, N., De Haan, A., 2008. Hydraulic pressing of oilseeds: experimental determination and modeling of yield and pressing rates. *J. Food Eng.* 89, 8–16.
- Zhu, Y., Xu, J., Mortimer, P.E., 2011. The influence of seed and oil storage on the acid levels of rubber seed oil, derived from *Hevea brasiliensis* grown in Xishuangbanna, China. *Energy* 36, 5403–5408.