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Recovery of Bio-Oil from Industrial Food Waste by Liquefied Dimethyl Ether for Biodiesel Production

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Abstract: The development of new energy sources has become particularly important from the perspective of energy security and environmental protection. Therefore, the utilization of waste resources such as industrial food wastes (IFWs) in energy production is expected. The central research institute of electric power industry (CRIEPI, Tokyo, Japan) has recently developed an energy-saving oil-extraction technique involving the use of liquefied dimethyl ether (DME), which is an environmentally friendly solvent. In this study, three common IFWs (spent coffee grounds, soybean, and rapeseed cakes) were evaluated with respect to oil yield for biodiesel fuel (BDF) production by the DME extraction method. The coffee grounds were found to contain 16.8% bio-oil, whereas the soybean and rapeseed cakes contained only approximately 0.97% and 2.6% bio-oil, respectively. The recovered oils were qualitatively analysed by gas chromatography-mass spectrometry. The properties of fatty acid methyl esters derived from coffee oil, such as kinematic viscosity, pour point, and higher heating value (HHV), were also determined. Coffee grounds had the highest oil content and could be used as biofuel. In addition, the robust oil extraction capability of DME indicates that it may be a favourable alternative to conventional oil extraction solvents.

Keywords: industrial food waste (IFW); bio-oil; biodiesel fuel (BDF); dimethyl ether (DME)

1. Introduction

Much effort has been devoted to developing methods for the production of biodiesel fuel (BDF) from biomass because of increasing concerns related to energy security and environmental protection. Among the resources derived from biomass, the properties of BDF from vegetable oils are well suited for diesel engines [1]. Therefore, vegetable oils can serve as an environmentally friendly alternative source of diesel fuel. Hence, edible oil plants such as soybean have been applied for the production of BDF in some countries [2,3]. In addition, inedible oils such as derived from baobab seed and *Firmiana platanifolia* have also been proposed as suitable feedstocks to produce BDF [4,5]. In addition, the utilization of aquatic plants such as algae as potential energy sources of bio-fuel has recently attracted particular attention [6]. Although aquatic algae have many advantages compared to terrestrial biomass, the production costs of bio-fuel from algae remain a substantial bottleneck to their large-scale use, and their commercial application is still under consideration [7]. Alternatively, owing to their availability and relatively low costs of production, the effective utilization of current industrial food wastes (IFWs) for the production of BDF is expected [8,9].

Much attention has been paid to the production of BDF from both edible and inedible oil feedstocks and from waste oil. However, another valuable resource remains: industrial oily feedstock waste. The production of oily industrial waste feedstock has increased in recent years. However, at present, the utilization of IFWs for the production of BDF is economically handicapped due to their relatively low oil contents, and there is currently no particularly effective method to recover the oil contained in such resources.

The CRIEPI has recently developed an energy-saving oil extraction technique involving the use of liquefied dimethyl ether (DME) [10]. This technique is both energy efficient and environmentally friendly because of the following unique properties of DME: (i) high affinity for oily compositions and partial miscibility with water [11]; (ii) low boiling point (−24.8 °C) and stability at normal temperatures (*i.e.*, DME in mixture can be separated from water to evaporate and recycle [12]; and (iii) it is a safe and biodegradable solvent for the production of foodstuffs [13]. Studies using pilot-scale equipment have been carried out, the energy-saving characteristics of this technique have been verified, e.g. in the case of dewatering of industrial green tea waste by using bench-scale equipment, the DME can be recycled under an operation pressure of 0.51 MPa at 10–30 °C [14]. This DME-based extraction method has also been used to recover the oily substances from a series of feedstocks [15–17]. To provide fundamental research toward the future commercial application of this technique, in this study, three major IFWs (spent coffee grounds, soybean, and rapeseed cakes) were investigated for oil recovery by using the lab-scale DME extraction method. The annual global production of these IFWs is shown in Table 1. As representative edible oil waste products, the global production of soybean and rapeseed cakes is extremely high [18]. Furthermore, approximately 6 million tons of spent coffee grounds are produced annually at beverage factories [19].

Table 1. Global annual production of industrial food wastes (IFWs) [20] and current disposals/utilization.

Meals	Production (MT) (Million tons per year)			Current disposal/utilization
	2011	2012	2013	
Coffee [(a)]	6.04	6.52	6.31	Fertilizer [21,22]; combustion (Silva *et al.* [22], 1998)
Copra	1.82	1.95	1.85	Feed [23]
Cottonseed	15.64	15.64	15.51	Feed [24]
Palm Kernel	7.22	7.76	8.29	Paper industry [25]
Rapeseed	35.65	36.95	38.62	Feed [26]
Soybean	180.42	180.95	188.15	Feed [27]; functional food (Wang *et al.* [27], 2013)
Total	246.79	249.77	258.73	-

(a): The production of coffee meal is estimated by the coffee production [20] and 30% of the weight of the coffee solubilized in water [28].

In the present work, we recovered oil from the three representative IWFs using DME to determine the recoverable contents of oil and the optimal ratio of DME to biomass. The extracted oils were converted to their fatty-acid methyl esters (FAMEs, *viz*. BDF) and were analysed qualitatively. As the oil contents of soybean and rapeseed cake are low and the size of the lab-scale apparatus is small, only the FAMEs derived from coffee grounds were subjected to further analysis for characterising the corresponding BDF properties. The proximate and ultimate analysis of coffee ground residues and the contents of K, N, and P in the residues of soybean and rapeseed cakes were determined to establish their potential utilisation in bio-fuel production and agricultural practice.

2. Results and Discussion

2.1. Recoverable Oil Content in the Industrial Food Wastes

The characteristics of oils extracted by liquefied DME from these biomasses are shown in Figure 1. Here, the consumption of DME (horizontal axis) is expressed as the relative ratio to the dry weight of samples. The maximum oil recovery rates by DME extraction of coffee grounds, soybean, and rapeseed cakes were 16.8% ± 1.0%, 0.97% ± 0.05%, and 2.6% ± 0.2%, respectively. To reach the maximum oil extraction yield, the consumption of DME was increased 69.5 times, 33.6 times, and 30.1 times for the coffee grounds, soybean, and rapeseed cakes, respectively, relative to dry weight. The difference in DME consumption between these biomasses is likely due to their different water and oil contents; in particular, coffee grounds have an especially high water content, and therefore dissolved more with increasing amounts of DME. Previous work has also found low amounts of oil remaining in the soybean and rapeseed cakes, after using both mechanical and organic solvent extraction methods [29,30]. Hexane is most often used as the extraction solvent in current industrial food oil extraction procedures [18], whereas the present results indicate that liquefied DME is more powerful than hexane for the extraction of oil from oil plants. In fact, the utilization of liquefied DME as a green solvent in the food industry has been approved by the European Food Safety Authority [13]. Therefore, because of its unique properties, DME is a promising oil extraction solvent for IFWs.

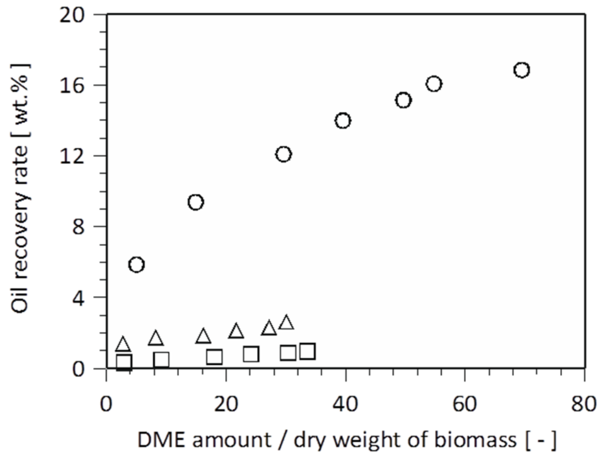
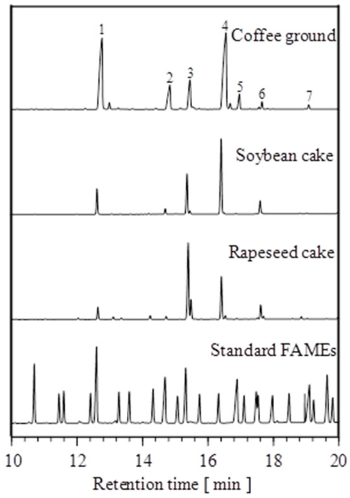


Figure 1. Oil recovery from IFWs using liquefied dimethyl ether (DME). The following IFWs were used: ○ coffee grounds; △ rapeseed cake; ▫ soybean cake.

2.2. Properties of Fatty-Acid Methyl Esters and Dimethyl Ether-Extracted Residues

As shown in Figure 2, seven fatty acids were clearly detected in the oil extracted by DME from the IFWs. The extracted oil consisted of saturated fatty acids (SFAs: palmitic acid, stearic acid, and eicosanic acid), mono-unsaturated fatty acid (MUFA: oleic acid), and polyunsaturated fatty acids (PUFAs: linoleic acid, linolenic acid, and eicosapentanoyl acid). As expected, fatty acids of carbon chain lengths between C_{16} and C_{18} were predominant in the oils extracted from soybean and rapeseed. Besides the C_{16-18} chain length, the long-chain fatty acids eicosanic acid and eicosapentanoyl acid were present in the coffee oil. The gas chromatography-mass spectrometry (GC-MS) analysis showed that the bio-oils extracted from the three IFWs by the DME extraction method were predominantly a mixture of SFA and MUFA components, which are suitable for obtaining good-quality BDF. Herein, rational use of the by-product glycerol should be considered. A recent study has reported microbial conversion of ethanol from BDF-derived glycerol [31]. Because of the small amount of sample, we only measured the kinematic viscosity, pour point, and higher heating value (HHV) for coffee FAMEs, which were 4.81 $mm^2 \cdot s^{-1}$, −7.5 °C, and 40.8 $MJ \cdot kg^{-1}$, respectively. The limitation values for these factors for BDF production, based on European BDF Standards (EN 14213), are 3.5–5.0 $mm^2 \cdot s^{-1}$, 0 °C max, and 35.0 $MJ \cdot kg^{-1} \cdot$ min [32].

The results of the proximate analysis, the main elemental compositions of coffee ground residue, and the contents of P, K, and N of the other two biomass residues are shown in Table 2. The ash yield, volatile matter, and fixed carbon of the coffee grounds were 1.9%, 81.1%, and 17.0%, respectively. The HHV of the coffee ground residue was 21.1 $MJ \cdot kg^{-1}$, indicating that it has sufficient caloric value to be used as a bio-solid fuel for blending combustion of coal. In comparison with coffee grounds, the residues of soybean and rapeseed showed 0.79%–1.37% of P, 2.29%–1.37% of K, and 8.73%–6.80% of N remaining. Therefore, the residues of soybean and rapeseed are potential nutrient source for agriculture. In fact, such IFWs have been historically applied for agricultural utilization.



Peak No.	Methyl ester of fatty acids	Chain length
1	Palmitic acid	C16:0
2	Stearic acid	C18:0
3	Oleic acid	C18:1
4	Linoleic acid	C18:2
5	Eicosapentaenoic acid	C20:5
6	Linolenic acid	C18:3
7	Eicosanic acid	C20:0

Figure 2. Gas chromatography analysis of the fatty-acid methyl esters (FAMEs) from IFWs. The presence of various methyl esters is shown in the inset table.

Table 2. Properties of residues and FAMEs derived from IFWs.

Analysis	Coffee Grounds		Soybean Cake	Rapeseed Cake
(wt % dry basis)	Residue	FAMEs	Residue	Residue
Ash yield	1.9	-	-	-
Volatile matter	81.1	-	-	-
Fixed carbon	17.0	-	-	-
C	51.5	-	-	-
H	6.97	-	-	-
N	2.43	-	-	-
O	37.1	-	-	-
S	0.15	-	-	-
P	0.09	-	0.79	1.37
K	0.22	-	2.29	1.37
N	2.51	-	8.73	6.80
Kinematic viscosity at 40 °C ($mm^2 \cdot s^{-1}$)	-	4.81	-	-
Pour point (°C)	-	−7.5	-	-
Higher heating value (HHV) ($MJ \cdot kg^{-1}$)	21.1	40.8	-	-

2.3. Possible Application of the Dimethyl Ether Extraction Method for Industrial Food Wastes

As shown in Table 1, the total production of these IFWs has increased continuously in recent years. Most of these IFWs showed considerable oil contents remaining after the industrial process [29,30,33]. Currently, these IFWs are disposed of and/or utilized as fertilizer, animal feed, and even as functional foods. Palm kernel and coffee grounds can also be used directly in the paper industry as solid fuels. Our current results revealed that the DME extraction method could efficiently recover bio-oil from the tested IFWs, especially from the coffee grounds, with a high oil recovery rate. Therefore, this method may provide a new approach to improve the traditional disposal and/or reutilization of these IFWs. A schematic overview of the possible utilization of the DME extraction method in the food and bio-fuel production industry is shown in Figure 3. In the proposed approach, the wet IFWs are first extracted with the DME extraction method; the recovered oil can further convert to a liquid bio-fuel such as BDF. The solid residue obtained after DME extraction can be treated by traditional disposal and/or reutilization methods. The water present contained in the IFWs is substantially removed during DME extraction. Only 1.8%, 0.9% and 0.7% water were remained in coffee ground, soybean and rapeseed cakes. Some residues of IFWs, such as coffee grounds obtained after DME extraction, can be a good source of bio-solid fuel. Furthermore, considering the expected lack of water supply in the future [34], the removed water may then become a potential resource for agricultural utilization. In fact, agricultural irrigation using such industrial waste water had been reported elsewhere [35].

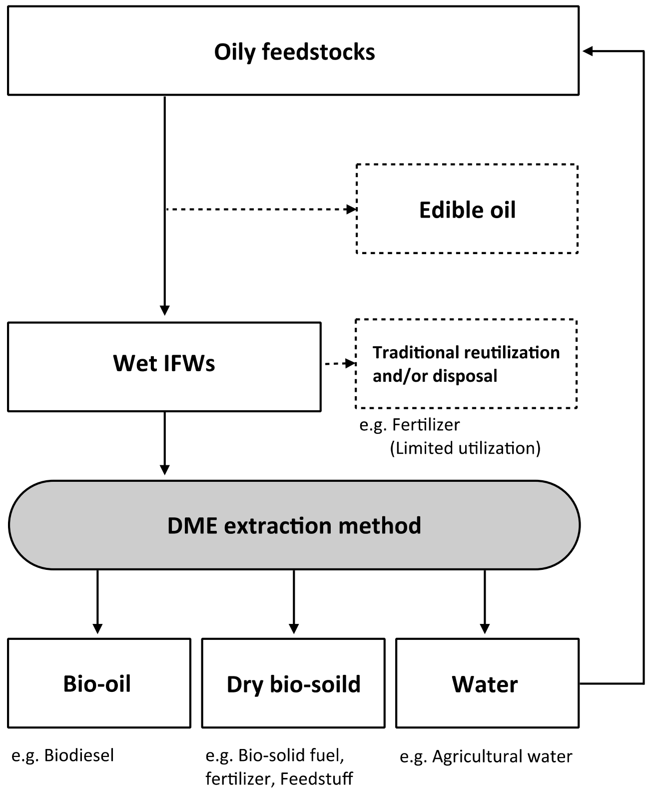


Figure 3. Proposed (**solid line**) and traditional (**broken line**) approaches for the disposal and reutilization of IFWs.

3. Materials and Methods

3.1. Materials

The soybean and rapeseed cakes were obtained from Japan agricultural cooperatives. The water contents of soybean and rapeseed cakes were 8.8% and 6.0%, respectively. The spent coffee grounds (pulverized coffee bean) were supplied by a Japanese brewing company. The water content of coffee grounds was 42.0%.

3.2. Dimethyl Ether extraction

The experimental apparatus has been described in detail in our previous paper [15]. In brief, the apparatus consists of two main parts: an extraction column (diameter, 11.6 mm; length, 190 mm; HPG-10-5, Taiatsu Techno Corporation; Saitama, Japan) and a storage vessel for the mixture of DME, oil, and water (HPG-96-3, Taiatsu Techno Corporation, Tokyo, Japan). The extraction column was loaded with the test sample. At the column outlet, the extracted oil passed through a filter (pore diameter < 0.65 μm). The DME flow rate was 10 ± 1 $cm^3 \cdot min^{-1}$, and the extraction temperature and pressure were 20 °C and 0.51 MPa, respectively.

3.3. Transesterification of Bio-Oil

Transesterification of the extracted oil to FAMEs was conducted by employing a 6:1 molar ratio of methanol to oil for 1 h at 60 °C with 1.5 wt % KOH as a catalyst. After completion of the reaction, the mixture was cooled to room temperature and kept stationary until a good separation of the two phases was achieved. The upper phase consisted of FAMEs and the lower phase contained glycerol, excess methanol, catalyst, and soaps formed during the reaction. After separation of the two phases by decantation, the methanol was removed from the FAMEs layer at 80 °C, and the remaining catalyst was removed by successive washing with distilled water. Finally, the residual water was removed by Na_2SO_4.

3.4. Analysis of Fuel Properties

The proximate analysis, ultimate analysis, and HHV determination were carried out for the coffee ground residues to determine their applicability to bio-fuel production. The contents of P, K, and N were measured for the residues of all three biomasses to determine their potential for agricultural utilization. The kinematic viscosity, pour point, and HHV were analysed for the FAMEs of coffee grounds obtained by DME extraction. The analytical methods of the Japanese industrial standard (JIS) were adopted, which were also used in our previous study [17]. The contents of P, K, and N were determined according to the methods of JIS M8801 (P and K) and JIS M8819 (N). The kinematic viscosity and pour point were determined according to JIS K 2283 and JIS K 2269.

For qualitative analysis, the retention times and mass spectra of the detected FAMEs were compared with those of standard chemicals (Supelco 37 Component FAME Mix, Sigma-Aldrich; St. Louis, MO, USA). GC-MS was performed on a GC: 6890N, MS: 5975B system (Agilent Technologies Inc.; Foster City, CA, USA) with an HP-1 column (15 m × 0.25 mm internal diameter (i.d.); Agilent Technologies Inc.).

4. Conclusions

Three oily IFWs were investigated as candidate oil resources for bio-fuel production. From the results, the following conclusions can be drawn: coffee grounds have the highest oil content among the three candidates and are suitable for BDF production. Although the soybean and rapeseed cakes have low oil contents, the results showed that the oil extraction capability of DME is robust. Therefore, the DME extraction method is a promising alternative to conventional oil extraction methods. This study provides a novel approach for the reutilization of oily IFWs. For the effective use of IFW resources, our proposed method should be further evaluated in other IFWs as well as value-added components in the IFWs tested herein.

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Author Contributions: Peng Li and Kiyoshi Sakuragi contributed to the overall idea interpretation, data analysis and writing of the manuscript. The research direction was provided by Maromu Otaka and Hisao Makino.

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

Abbreviations

IFWs	Industrial food wastes
CRIEPI	Central Research Institute of Electric Power Industry
DME	Dimethyl ether
BDF	Biodiesel fuel
FAMEs	Fatty-acid methyl esters
MUFA	Mono-unsaturated fatty acid
GC-MS	Gas chromatography-mass spectrometrys

References

1. Thanh, L.T.; Okitsu, K.; Boi, L.V.; Maeda, Y. Catalytic technologies for biodiesel fuel production and utilization of glycerol: A review. *Catalysts* **2012**, *2*, 191–222. [CrossRef]
2. International Energy Agency (IEA). Biofuels for transport. Available online: http://www.cti2000.it/Bionett/All-2004-004%20IEA%20biofuels%20report.pdf (accessed on 11 November 2014).

3. Dagostin, J.L.A.; Carpiné, D.; Corazza, M.L. Extraction of soybean oil using ethanol and mixtures with alkyl esters (biodiesel) as co-solvent: Kinetics and thermodynamics. *Ind. Crops Prod.* **2015**, *74*, 69–75. [CrossRef]
4. Modiba, E.; Osifo, P.; Rutto, H. Biodiesel production from baobab (*Adansonia digitate L.*) seed kernel oil and its fuel properties. *Ind. Crops Prod.* **2014**, *59*, 50–54. [CrossRef]
5. Zhang, H.; Zhou, Q.; Chang, F.; Pan, H.; Liu, X.F.; Li, H.; Hu, D.Y.; Yang, S. Production and fuel properties of biodiesel from *firmiana platanifolia L.f.* as a potential non-food oil source. *Ind. Crops Prod.* **2015**, *76*, 768–771. [CrossRef]
6. Liam, B.; Philip, O. Biofuels from microalgae—A review of technologies for production processing, and extractions of biofuels and co-products. *Renew. Sustain. Energy Rev.* **2010**, *14*, 557–577.
7. Grima, E.M.; Belarbi, E.-H.; Fernàndez, F.G.A.; Medina, A.R.; Chisti, Y. Recovery of microalgal biomass and metabolites: Process options and economics. *Biotechnol. Adv.* **2003**, *20*, 491–515. [CrossRef]
8. Romano, S.D.; Sorichetti, P.A. *Dielectric Spectroscopy in Biodiesel Production and Characterization*; Springer-Verlag: London, UK, 2011.
9. Zhou, A.; Thomson, E. The development of biofuels in Asia. *Appl. Energy* **2009**, *86*. [CrossRef]
10. Li, P.; Makino, H. Liquefied dimethyl ether: An energy-saving, green extraction solvent. In *Alternative Solvents for Natural Products Extraction*; Chemat, F., Abert, V.M., Eds.; Springer: Berlin/Heidelberg, Germany, 2014; pp. 91–106.
11. Holldorff, H.; Knapp, H. Binary vapor-liquid-liquid equilibrium of dimethyl ether-water and mutual solubilities of methyl chloride and water: Experimental results and data reduction. *Fluid Phase Equilib.* **1988**, *44*, 195–209. [CrossRef]
12. Wu, J.; Zhou, Y.; Lemmon, E.W. An equation of state for the thermodynamic properties of dimethyl ether. *J. Phys. Chem. Ref. Data* **2011**, *40*. [CrossRef]
13. European Food Safety Authority (EFSA). Scientific opinion of the panel on food contact materials, enzymes, flavourings and processing aids (CEF). *EFSA J.* **2009**, *984*, 1–13. Available online: http://www.efsa.europa.eu/sites/default/files/scientific_output/files/main_documents/1305.pdf (accessed on 23 July 2009).
14. Kanda, H.; Li, P.; Makino, H. Production of decaffeinated green tea leaves using liquefied dimethyl ether. *Food Bioprod. Process.* **2013**, *91*, 376–380. [CrossRef]
15. Kanda, H.; Li, P.; Goto, M.; Makino, H. Energy-saving lipid extraction from wet *Euglena gracilis* by the low-boiling-point solvent dimethyl ether. *Energies* **2015**, *8*, 610–620. [CrossRef]
16. Kanda, H.; Li, P. Simple extraction method of green crude from natural blue-green microalgae by dimethyl ether. *Fuel* **2011**, *90*, 1264–1266. [CrossRef]
17. Li, P.; Kanda, H.; Makino, H. Simultaneous production of bio-solid fuel and bio-crude from vegetal biomass using liquefied dimethyl ether. *Fuel* **2014**, *116*, 370–376. [CrossRef]
18. Seth, S.; Agrawal, Y.C.; Ghosh, P.K.; Jayas, D.S.; Singh, B.P.N. Oil extraction rates of soybean using isopropyl alcohol as solvent. *Biosyst. Eng.* **2007**, *97*, 209–217. [CrossRef]
19. Mussatto, S.I.; Carneiro, L.M.; Silva, J.P.A.; Roberto, I.C.; Teixeira, J.A. A study on chemical constituents and sugars extraction from spent coffee grounds. *Carbohydr. Polym.* **2011**, *83*, 368–374. [CrossRef]
20. United States Department of Agriculture, USDA. Available online: http://apps.fas.usda.gov/psdonline/psdReport.aspx?hidReportRetrievalName=Table+01%3a+Major+Oilseeds%3a+World+Supply+and+Distribution+%28Commodity+View%29+++++++++++++++++++++++++++&hidReportRetrievalID=531&hidReportRetrievalTemplateID=5 (accessed on 1 April 2015).
21. Zuorro, A.; Lavecchia, R. Polyphenols and energy recovery from spent coffee grounds. *Chem. Eng. Trans.* **2011**, *25*, 285–290.
22. Silva, M.A.; Nebra, S.A.; Silva, M.J.M.; Sanchez, C.G. The use of biomass residues in the Brazilian soluble coffee industry. *Biomass Bioenergy* **1998**, *14*, 457–467. [CrossRef]
23. O'Doherty, J.V.; McKeon, M.P. The use of expeller copra meal in grower and finisher pig diets. *Livest. Prod. Sci.* **2000**, *67*, 55–65. [CrossRef]
24. Fombad, R.B.; Bryant, M.J. An evaluation of the use of cottonseed cake in the diet of growing pigs. *Trop. Anim. Health Prod.* **2004**, *36*, 295–305. [CrossRef] [PubMed]
25. Singh, P.; Sulaima, O.; Hashim, R.; Peng, L.C.; Singh, R.P. Using biomass residues from oil palm industry as a raw material for pulp and paper industry: Potential benefits and threat to the environment. *Environ. Dev. Sustain.* **2013**, *15*, 367–383. [CrossRef]

26. Huuskonen, A.; Huhtanen, P.; Joki-Tokola, E. Evaluation of protein supplementation for growing cattle fed grass silage-based diets: A meta-analysis. *Animal* **2014**, *8*, 1653–1662. [CrossRef] [PubMed]
27. Wang, H.; Zhang, S.; Sun, Y.; Dai, Y. ACE-Inhibitory peptide isolated from fermented soybean meal as functional food. *Int. J. Food Eng.* **2013**, *9*, 1–8. [CrossRef]
28. Cruz, M.M.; Cardoso, L.; Fernandes, M.; Oliveira, E.; Mendes, P.; Baptista, S. Espresso coffee residues: A valuable source of unextracted compounds. *J. Agric. Food Chem.* **2012**, *60*, 7777–7784. [CrossRef] [PubMed]
29. Wiemer, H.J.; Altes, F.W.K.A. *Small Scale Processing of Oilfruits and Oilseeds*; Gesellschaft fur Technische Zusammenarbeit (GTZ): Eschborn, Germany, 1989.
30. Li, S.; Zhu, D.; Li, K.; Yang, Y.; Lei, Z.; Zhang, Z. Soybean curd residue: Composition, utilization, and related limiting factors. *ISRN Ind. Eng.* **2013**, *2013*. [CrossRef]
31. Suzuki, T.; Nishikawa, C.; Seta, K.; Shigeno, T.; Nakajima-Kambe, T. Ethanol production from glycerol-containing biodiesel waste by *Klebsiella variicola* shows maximum productivity under alkaline conditions. *New Biotechnol.* **2014**, *31*, 246–253. [CrossRef] [PubMed]
32. Gerhard, K. Analyzing biodiesel: Standards and other methods. *J. Am. Oil Chem. Soc.* **2006**, *83*, 823–833.
33. Jenkins, R.W.; Stageman, N.E.; Fortune, C.M.; Chuc, C.J. Effect of the type of bean, processing, and geographical location on the biodiesel produced from waste coffee grounds. *Energy Fuels* **2014**, *28*, 1166–1174. [CrossRef]
34. Ruane, J.; Sonnino, A.; Steduto, P.; Deane, C. Coping with water scarcity: What role for biotechnologies? FAO Land and Water Discussion Paper No. 7. Available online: http://www.fao.org/docrep/011/i0487e/i0487e00.htm (accessed on 28 January 2009).
35. Singh, A.K.; Mahato, M.K.; Neogi, B.; Tewary, B.K.; Sinha, A. Environmental geochemistry and quality assessment of mine water of Jharia coalfield, India. *Environ. Earth Sci.* **2012**, *65*, 49–56. [CrossRef]