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Circulatory Management of Nutritional Substance Growing Sunflower and Extracting Nutrition by Hot-compressed Water Treatment

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Sunflowers are grown as an ornamental plant and a catch crop beside an oilseed crop in Japan. Seed residues after oil milling are recycled as a feed for livestock and a fertilizer. After harvesting, crop residue such as stem and leaves are returned to the soil by the tillage in conventional cultivation. This report discusses the appropriate circulatory management of crop residues and plant nutrition considering them as a new commodity and plant nutrients resource for activating small agriculture.
To study the characteristics of the nitrogen uptake from soil, sunflower cultivar named Hybrid Sunflower was grown with fixed row distance of 70 cm and varying hill distance of 10, 20, 30, 40 and 50 cm in a 5 m * 5m plot at a university farm, Tokyo, Japan. Growth survey was carried out every week. Sunflower whole crops sampled at each plot were dried in the oven at 70 ºC for 1 day soon after the blanching treatment and stored until the extraction experiment.
Sunflower sample at the growth stage of after flowering had the largest mass compared with the stage of before flowering and seed harvesting. Total dried matter of whole crop in 10cm-plot was the largest among the planting density conditions for each growth stage. The dried matter of crop residue at the growth stage of seed harvesting was 613, 408, 323, 281 and 279 g/m^2 for the plot of 10, 20, 30, 40 and 50 cm, respectively. Nitrogen contained in sunflower stem was 2.5 to 5.5 g-N/m^2 and that in seed was almost double, 5.9 to 7.5 g-N/m^2. Sunflowers were processed to extract nitrogen by the hot-compressed water (HCW) treatment. Ground sample of sunflower stem mixed with water was heated at temperature of 180, 200 and 220 ºC with gas pressure of 2 MPa in a pressure tight reactor for 5 and 30 min to release nitrogen from the solid fibre. Sample was separated into the solid matter fraction and the liquid matter fraction after the treatment. Extracted nitrogen as liquid matter was 37.9, 45.5 and 49.4 % at temperature of 180, 200 and 220 ºC, respectively. Approximately 40 to 50 % of nitrogen contained in sunflower stem was recovered as the liquid matter. The liquid matter can be returned to the soil as a fertilizer while the solid matter containing cellulose and hemi-cellulose can be used as a raw material for bioethanol production.

1. Introduction

1.1 Crop residue management

Crop residues such as rice straw is multi useful resource to supply several agricultural materials which have been used for mulching, feeding and composting. Recently crop residues are expected as raw material of biofuels because edible parts of crops may not be used to produce biofuels anymore in view of world food situation. Japan Institute of Energy (2007) has published the amount of crop residues in Japan as follows; rice 1.4, wheat 1.3, maize 1.0 sugarcane 0.28 t/t-yield. Total amount of crop residues is estimated to be over 14 million ton, 100 PJ per year in Japan. Beside energy component, crop residues contain a lot of plant nutrients such as nitrogen, phosphorus and potassium. These components will be discharged as waste when the crop residue is used as a raw material of biofuel. Circulatory management of crop residues is becoming very important because plant nutrients should be returned to the agricultural fields without releasing to the environment. Many researchers have pointed out that losses of nitrogen from arable land to the aquatic environment (nitrate leaching) or the atmosphere (gaseous losses) have increased in the last few decades

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(Jeuffroy et al., 2002). Matsumura and Watanabe (2001) stated that the application of manure or compost has long been recognized as an important technique for improving or maintaining soil fertility, because it improves soil physicochemical properties and biological diversification.
Figure1 shows the concept of circulatory management for crop residues and plant nutrients. The whole crops including grains transported from the fields to a primary factory can be primarily processed to divide into the edible and inedible part. All wastes from the primary factory will be furtherly processed to make fertilizer and compost in the secondary process. These factories should be located in the countryside and plant nutrients can be easily recycled in the small circulatory system. It is difficult to return these nutrients to the fields once they go out to a large distribution system like food system.

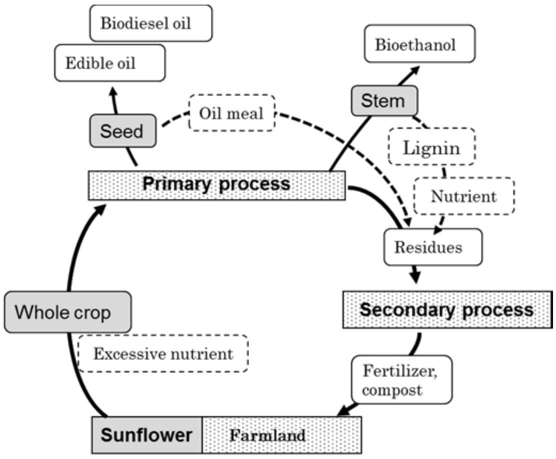

Figure 1: Circulatory management of crop residues and plant nutrients.

Some pretreatments for separating useful materials and components from crop residues in the primary process have been studied by many researchers. We focus on the hot-compressed water (HCW) treatment as a pretreatment for extracting plant nutrition from crop residues. Sasaki et al. (1998) have proposed super critical water (SCW) to hydrolyze cellulose rapidly and to recover glucose, fructose and oligomers from biomass. It uses in the range of temperature from 290 to 400 °C and high pressure at 25 MPa. Sakaki et al. (1998) have reported that hot compressed water in a batch reactor at temperatures between 250 and 405 ºC convert cellulosic biomass to raw materials for alcohol fermentation effectively. These methods show relatively high yield of hydrolysis product, however, the operation are not profitable and cannot be performed usually. Yu et al. (2014) have investigated structural features of rice straw pretreated by hot-compressed water (HCW) from 140 to 240 ºC for 10 or 30 min on the condition of enzymatic hydrolysis. Ngamprasertsith et al. (2015) reported that the HCW-pretreatment at 180 ºC, 2 MPa for 20 min was suitable as a pretreatment for subsequent enzymatic saccharification of Thai rice straw. Zhou et al. (2014) revealed that the parenchyma-type second cell-wall structure of the corn stover was almost completely removed at 185 ºC using a scanning electron microscopy. Weinwurm et al. (2016) discussed the optimization of the combined HCW and the ethanol organosolv pretreatment to release carbohydrates from wheat straw. In this research project, we assume that the HCW treatment is an appropriate pretreatment of crop residues as primary process in the countryside factory.

1.2 Sunflower features

Sunflowers are grown as an ornamental plant and a catch crop beside an oilseed crop in Japan. Cropping acreage of sunflower is statistically not large, however, we can find it everywhere because of its strong growth potential. Sunflower has also powerful uptake abilities of plant nutrients from soil. Some trials to remove the excessive nutrients in the soil have been executed by using sunflower cultivation. Sunflower grows quickly in the summer season hence it is known as a fallow crop. We employ sunflower as a test crop in this research for these reasons.

2. Materials and methods

2.1 Sunflower cultivation

Sunflower (Kaneko seed, Hybrid sunflower) was used as a test crop. Planting density of sunflower was varied from 2.8 to 14.2 hills per square meters with fixed row distance of 70 cm and five different hill distance of 10, 20, 20, 30, 40 and 50 cm. Area of an experimental plot is 25 m^2, 5 m x 5 m, and three replicates. Chemical nitrogen fertilizer was applied to each plot at the rate of 10 g-N/m^2 (100 kg-N/ha) before seeding. Other nutrients of phosphorus and potassium were applied at the same rate of 10 g/m^2 to each plot. Growth observation was executed every week on plant length, stem diameter and number of leaves, and sunflower was sampled in the growth stage of flowering (52 days after seeding), after flowering (63 days after seeding) and harvesting time (96 days after seeding). Seeding was on July 4 and harvesting was on October 8, 2014.

2.2 Sample of sunflower

Sampled sunflowers from the field were measured on their fresh weight and dried matter. Sunflowers were dried with an electric oven at 90 ºC for 30 min as blanching soon after sampling and continued drying at 70 ºC for 1 day. Dried matter of the individual sample was measured after dividing into the organ parts of stem, leaf, calyx and seed. Dried matter was stored in a sample bin under the dehumidified condition after crushing with a small pulverizer.

2.3 Hot-compressed water treatment

In this research, a separating operation of plant nutrients, nitrogen, from crop residue was examined by the hot-compressed water (HCW) treatment in relatively low range of temperature less than 250 ºC. The HCW treatment has been tested for degrading the fibrous biomass because the treatment has good features; not much heat energy, available to wet material and strong degrading power without chemicals. Figure 2 illustrates the structure of the HCW treatment apparatus (Parr, Parr 4766). A reactor in 300 mL capacity tolerable to pressure of 20 MPa and temperature of 300 ºC is covered with a heater and connected to a nitrogen high-pressure gas tube. The inside pressure is supplied and adjusted with nitrogen gas to avoid boiling and combustion. The sample liquid in the reactor never boils and keeps liquid state when the inside pressure of reactor is over the saturation water vapor pressure at high temperature. Therefore, the HCW treatment system can save the phase transition enthalpy from liquid to vapor phase.

To find the sufficient condition for the extracting operation of plant nutrients, the following variations of temperature and retention time were examined under the fixed pressure of 2 MPa; temperature: 180, 200 and 220 ºC; retention time: 5 and 30 min. Dried sample of 5 g mixed with 50 mL water was used as a test material. The sample was heated up to the set temperature and kept for the retention time with a temperature controller (KEYENCE, TF4-10V) and thermocouple sensor. The reactor was cooled with water soon after passing the retention time. The solid fraction was separated from the cooled sample by suction filtration with a glass disc (Shibata, 1GP100) and dried at 105 ºC with an oven.

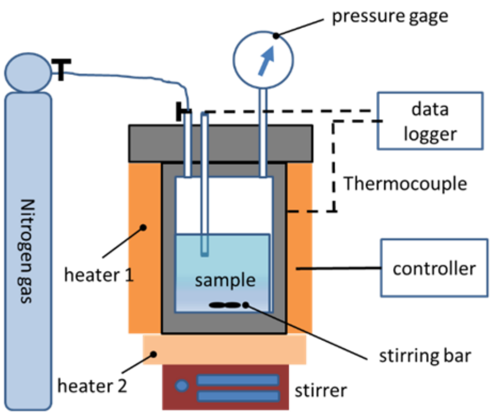

Figure 2: Hot-compressed water treatment apparatus.

2.4 Nitrogen measurement

Total nitrogen was measured with a C-N analyser (Yanaco, MT-600) by combustion method. Test sample of 0.1 g was combusted at 950 ºC for 5 min in the furnace and the concentration of N_2 gas was determined with TCD detector referring to hippuric acid.

3. Results and discussions

3.1 Sunflower growth and uptake nitrogen

Changes in plant length of sunflower for each plot are shown in Figure 3. High planting density plot of 10cm in hill distance grew fast and low planting density plot of 50 cm grew late among the conditions. The stem diameter of sunflower at harvesting time had big differences among the conditions; 17.8, 20.1, 22.0, 23.5 and

25.4 mm for each planting density condition, respectively (Figure 4). Sunflower has large variation in morphological development until the harvesting time when the planting density is varied. Dried matter per unit area of sunflower at harvesting time is shown in Figure 5. High planting density plot of 10 cm in hill distance was the largest among the conditions. Individual sunflower in the 10 cm plot has tallest in height and thinnest in stem diameter, however, final biomass per unit area became larger than the others. Seed yield of the plot of 10, 20, 30, 40 and 50 cm in hill distance was 143, 150, 151, 156 and 184 g/m^2, respectively. Seed yield has a trend to increase when the planting density becomes lower. Crop residue consisting of stem, leaves and calyx decreased when the planting density was lowered. Amount of crop residue in the plot of 10, 20, 30, 40, 50 cm were 613, 408, 323, 281 and 279 g/m^2, respectively. Crop residue of the 10 cm plot was more than two times of the 50 cm plot. Total biomass including seed depended strongly on the planting density. The stiffness of sunflower stem was influenced also by the planting density because of stem diameter. Many stems in higher planting density plots were broken after typhoon passing because stems could not resist the strong wind of typhoon. In real cultivation, it should be considered how sunflower will not be damaged by typhoon in Japan if the planting density is high. Nitrogen content in stem including leaves, calyx and seed of sunflower per unit area at the stage of harvesting time is shown in Figure 6. Nitrogen content of seed increased when the planting density was lowered. Nitrogen content of stem and calyx in the plot of 10, 20, 30, 40 and 50 cm in hill distance was 5.53, 3.67, 2.92, 2.54 and 2.52 g-N/m^2, respectively, while its content in seed increased as 5.86, 6.12, 6.16, 6.40 and 7.54 g-N/m^2 with lowering planting density. Total nitrogen contents in stem and calyx of the 10 cm plot was 2.2 times of the 50 cm plot. Stem has a function of storing nitrogen so that the large capacity of stem results big flower and high seed yields. Malagoli et al. (2005) have reported in the rape seed experiment that the stem can also be considered as a buffer organ in which endogenous N mobilized from sink organs (lower leaves, taproot) is stored during the vegetative period and then used for pod filling. This reallocation of nitrogen during the seed filling period is reason why difference in the total nitrogen of sunflower is not as large as difference in biomass.

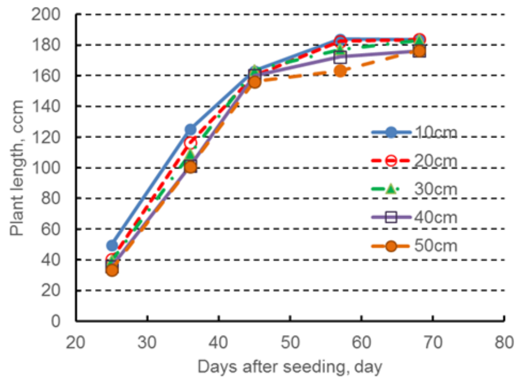

Figure 3: Change in plant length of sunflower.

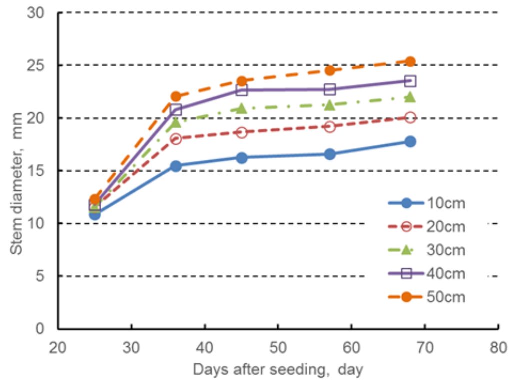

Figure 4: Change in stem diameter of sunflower

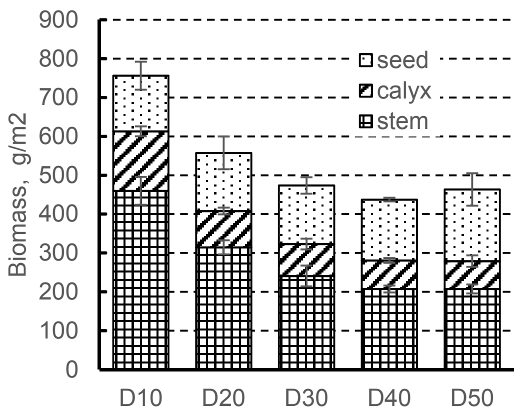

Figure 5: Dried matter of sunflower at harvesting time.

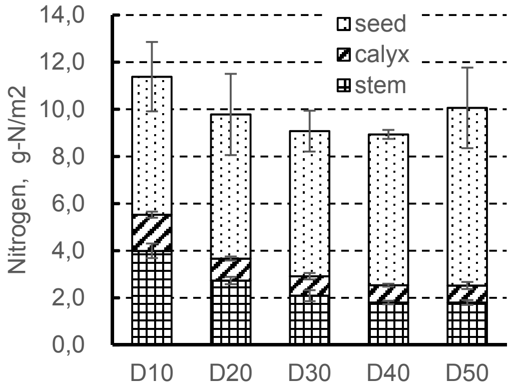

Figure 6: Nitrogen content in each part of sunflower

Nitrogen content of stem and calyx in the plot of 10 cm and 20 cm were significantly higher than the other plots with Tukey's multiple comparison in statistics. Management of nitrogen in crop residue of sunflower should be considered on the stem and calyx, and also that on the oil meal after oil milling because of high nitrogen content in seed. Total nitrogen contained in sunflower was nearly equal to the applied nitrogen to the soil as fertilizer before starting cultivation. Higher planting density may be reasonable if we aim the nitrogen uptake from the soil.

3.2 Nitrogen extraction from sunflower stem using HCW treatment

Extracted nitrogen from sunflower stem using the HCW treatment was recovered in liquid form and calculated with the following equation Eq(1).

$$Ex = \left(1 - \frac{m_{solid}}{M_{solid}}\right) \times 100 \tag{1}$$

where *Ex*: extraction ratio of nitrogen in liquid (%),
m_{solid}: solid dried mass left after HCW treatment (g),
M_{solid}: initial solid mass of sample (g).

Table 1 shows the result of the HCW treatment. The extraction ratio of nitrogen from sunflower stem increased with the rise of reactor temperature. The largest extraction ratio was obtained at 220 ºC both retention time of 5 min and 30 min. Comparing two retention time conditions, the extraction ratio in 30 min was larger than that in 5 min. The difference between two retention time conditions was relatively less than that between temperature conditions. Temperature at 220 ºC and retention time of 30 min gives the best condition in this experiment. However, the retention time of 5 min will be reasonable when the input energy cost should be controlled lower. Almost half nitrogen contained in sunflower stem can be extracted with the HCW treatment.
Table 2 shows the result of the HCW treatment using sample of each planting density plot at temperature of 180 ºC, pressure of 2 MPa and retention time of 5 min. About 31 - 39 % of nitrogen in sunflower stem was eluted to the liquid fraction by the HCW treatment. However, the trend of extraction ratio on the planting density conditions was not apparent in this experiment. The errors between these conditions may happen by the inhomogeneous sample of sunflower stem because the degradation rate of sample depends on the part of stem, pithy layer or cortical layer. Although the amount of recoverable nitrogen by the HCW treatment is not very large, nitrogen of 1 to 1.5 g/m^2 can be recycled when sunflower stem is used as a new industrial raw material. In the future, the research for the use of liquid fraction from the HCW treatment will be necessary to return the plant nutrition to farmland.

Table 1: Extraction ratio of nitrogen from sunflower stem using HCW treatment.

Condition	Extraction ratio of nitrogen in liquid (%)	
	5 min	30 min
180ºC-2MPa	37.9	42.6
200ºC-2MPa	45.5	46.4
220ºC-2MPa	49.4	50.4

Table 2: Extracted nitrogen from sunflower stem using HCW treatment at 180ºC-2MPa-5min.

	D10	D20	D30	D40	D50
Nitrogen in liquid (%) ±SD	34.0 ±5.7	31.3 ±5.3	34.7 ±6.2	32.7 ±0.9	39.3 ±4.1
Extracted nitrogen (mg-N/g-DM)	2.95	2.72	3.01	2.84	3.42

4. Conclusions

Crop residues are focused for use of a new industrial material such as biofuel. Circulatory management of crop residue and plant nutrients will be more important since depletion of plant nutrients resources is becoming serious.
Authors propose an above-mentioned system to utilize crop residues in the view of resource management and economical activation of rural area. The proposed primary process necessary for utilizing crop residues will be executable in the simple facility of a small factory located in countryside.

Sunflower is an attractive crop growing quickly anywhere in Japan and having strong ability of nutrient uptake from the soil. In this research, the effects of the planting density was discussed to clarify the reasonable condition for maximizing seed yields, crop residue and nitrogen uptake. The result of cultivation test shows that lower planting density leads to produce high seed yields, while higher planting density makes both crop residue and nitrogen uptake larger if the damages from typhoon is negligible. Reasonable planting density for producing high seed yields and high crop residue is 3 to 5 hills per square meters.
To extract nitrogen from crop residue, the hot-compressed water (HCW) treatment was examined by varying temperature and retention time conditions. Higher temperature condition brings high degradation of samples which indicate high extracting rate of nitrogen in the liquid matter. About 40% of nitrogen will be extracted with HCW treatment in the condition of temperature at 180 ºC, pressure at 2 MPa, retention time of 5 min. The primary processing of crop residue with the HCW treatment is available to recover nitrogen in a small circulation.

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