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The Study of Rotational Ultrafiltration System for Recovery of Spent Cutting Oil from Solar Photovoltaic Cell Manufacturing Process

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Abstract

The main problems of recovery cutting oil from spent waste are high viscosity of cutting oil and high content of nano-size particle. This study combined an innovative rotational circular-plate ultrafiltration membrane filter with a scraping device to recycle the cutting oil and remove particles fouling cake attached to the membrane surface, and was able to maintain cutting oil filtrate flux above 6.65 $l/m^2/hr$. Also, the proposed process is the practical solution for materials separation between highly viscosity liquid and fine particles even nano-size. The results show the filtrate of ultrafiltration membrane could meet the reuse requirements of less than 0.03% solid content. Analysis of blended oil characteristics under different blending ratios was conducted, showing the optimum blending ratio of recycled oil to new cutting oil was 6:4. The final production cost can be reduced over 27.4%. The process can achieve waste reuse ratio of greater than 77.2%.

Key Words: Rotational Ultrafiltration, Diethylene Glycol, Recycle, Silicon Sawing, Cutting Oil

1. Introduction

Solar energy is one of the most highly favored alternative energy to fossil fuels, however high polluted wastes are produced, such as spent cutting oil waste, during the manufacture of solar panels. During the ingot slicing stage, cutting oil is injected to the wire saw during slicing for cooling and lubrication purposes, as well as bringing the resulting silicon particles and impurities out of the cutting grooves.

Cutting oil typically contains high hardness silicon carbide (SiC) particles as a grinding material, which is supplemented with different mixing ratios of diethylene glycol (DEG). During the silicon ingot slicing process, the cutting oil quickly becomes contaminated by metal particles, silicon sawdust particles, and contaminated water. The used cutting oil turns into thick oil sludge with very high particle concentration and turbidity, losing its capacity to aid in the cutting process. Therefore, DEG is added continuously to the slicing equipment during the wire saw cutting step. Recycling and reusing cutting oil conforms to the cleaner process.

The purpose of this study is to verify cutting oil recovery capacity of ultrafiltration membrane system. In addition to monitoring the characteristics and chemical composition of the recovered cutting oil, different blending ratios of recycled cutting oil were also studied. It is to understand the extent of recycled cutting oil in conforming to the requirements of actual on-site applications, and to conduct the economic analysis of optimized utilization of recycled cutting oil.

1.1 Literature Review

DEG has the chemical formula of HO-CH_2CH_2-O-

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CH_2CH_2-OH and possesses similar chemical structure and properties to polyethylene glycol (PEG). DEG is a colorless, odorless, and viscous liquid that dissolves readily in water. SiC is a combination of silica and coke carbon. According to the manufacture, the cutting oil used for the solar wafer slicing process usually contains DEG and SiC in the ratio of: 1 L DEG to 3.2 kg SiC. DEG and SiC have a specific gravity of 1.1, so the weight ratio of DEG and SiC can be calculated as 25.6% and 74.4%, respectively. After the slicing process, some slicing debris is added to the used cutting oil, consisting mainly of silicon (Si) and iron (Fe). Traditionally, the solar cell manufacturers adopted the following methods to treat used cutting oil: extraction process to recover volatile solvents [1]; thermo-treatment for spent cutting oil as waste [2]; anaerobic digestion as wastewater [3]. However, the secondary pollution problems were associated with these methods.

DEG has very high viscosity, making the solid-liquid separation of fine particles and the recycling of cutting oil will be very difficult. Most studies focused on SiC and Si recovery because the high market prices of SiC and Si. The aluminum series chemicals was used successfully for separation of aluminum, SiC, and Si [4,5]. Some studies have added water or other solvents to dissolve PEG, followed by high speed centrifugation to separate the SiC and Si [6–9]. Increased the operating temperature to 60 °C to reduce the viscosity of the PEG, research showed the separation of PEG and particles (SiC and Si) can be improved [10]. Also, commercial ion-coupled plasma equipment was available for recovery of SiC and Si, but the recovery rate was reduced due to the presence of iron ions [11]. The studies listed above failed to address the recovery of DEG or PEG in used cutting oil. The main reason is that used cutting oil contains the SiC, Si, and iron particles over 36% by weight. It is very difficult to reduce this high particle content to less than 0.03% from spend cutting oil with highly viscosity.

With an operating temperature of 60 °C, solid content of 229.6 mg/L, self-made plate-type UF membrane device, cross-membrane pressure of 101.3 kPa, and membrane surface velocity of 0.05 m/s to recover cutting oil, this study was able to achieve membrane permeation flux of 7.68 $l/m^2/hr$ and the recovered filtrate was a clear liquid slightly yellow-green in color, confirmed to contain iron ions [12]. However, the 229.6 mg/L solid content was far less than the 36% (by weight) solid content under actual plant operation conditions.

2. Materials and Methods

Used spent cutting oil with the typical weight ratio of 25.5%, 74.3%, and 0.2% for DEG, SiC, and Si respectively, was used as the original feed for this experiment. The main recovery process involved two stages: primary filtration system and UF system. The primary filtration system recovered most of the SiC, and was followed by the UF system for further solid-liquid separation. The functions for each unit of the experiment were described in Figure 1 below.

2.1 UF Membrane and Scraping Rod Selection

Finding the proper filtration system was an essential step for exploring ways to recycle cutting oil. Hollow fi-

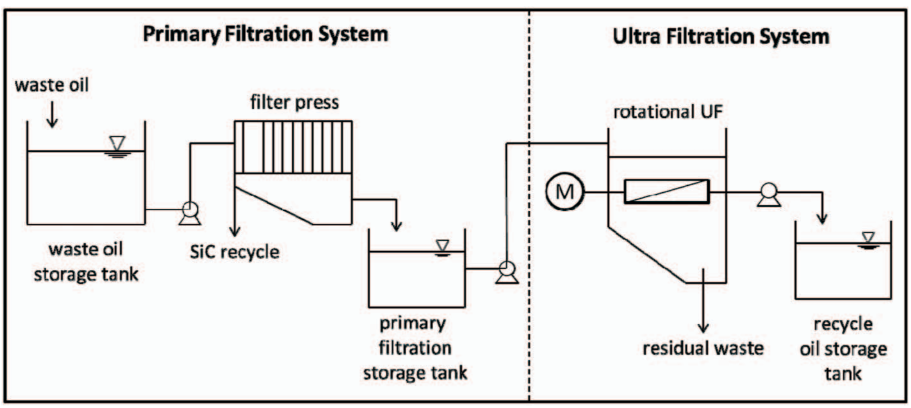

Figure 1. Schematic of the filtration system for DEG recycling.

ber membrane (Kuraray Aqua CO., LTD., Japan, Type-ML), tabulate membrane (Chyuan Bang CO., LTD., Taiwan, Kevin BN1016), and circular-plate UF membrane (New Century Membrane CO., LTD., Taiwan, NHV1-185-M80) were used in this experiment. The viscosity of cutting oil was high, causing the flux through the first two types of membranes to clog within 3 minutes. The circular-plate UF membrane without scraping device would clog after 10 minutes. Usually, the pressure could be increased to boost the driving force and allow fluids to pass through the membrane more quickly. The velocity of the fluids would prevent substances from attaching to the membrane. Unfortunately, cutting oil viscosity is too high to implement this method. Instead, a mechanical scraping mechanism was used to remove clogs and improve flux.

Pre-experimental scraping tests were conducted with plastic rods, plastic rods with sponges, wires, springs, and stainless steel rods. The first four materials became deformation and fractures due to high hardness of SiC and Si. Only the stainless steel rods could maintain its scraping function while not causing damage to the membrane. See Figure 2 for the equipment design.

2.2 Primary Filtration System

The primary filtration system consisted of three components defined below.

A. Waste oil storage tank: Container for storing waste/spent oil sludge.

B. Filter-press: The filter-press was connected to the waste oil storage tank using a waste oil feed pump. The filter-press removed and retained SiC particles larger than 5 μm from the waste cutting oil. Primary filtration was operated in batch mode at a temperature of 60 °C. Each batch contained about 190 L of cutting oil that will be filtered for 300 minutes through a filter cloth.

C. Primary filtration storage tank: A storage tank used to temporarily store filtrate released from the filter press.

2.3 UF System

The UF system consisted of two major components described below.

A. Rotational UF: Included the UF tank and the circular-plate UF membrane unit (PVDF material, with average pore size of 30 nm). The UF membrane unit was connected to a rotary drive mechanism and a pump. When the pump was activated, the resulting negative pressure caused the primary filtrate in the UF tank to go through the UF membrane unit and generate the recycled cutting oil. This UF membrane unit (see Figure 2) included a sludge guiding mechanism which was sandwiched between two UF membranes. It was in contact with the membranes so that it could remove the sludge adhered to the membranes and thus extended the UF unit's operating cycle. The UF unit's operating parameters included negative pressure at 50.6 kPa, UF module rotating at 12 rev/min, and cutting oil filtrate flux at above 6.65 $l/m^2/hr$.

B. Recycled oil storage tank: Contained recycled cutting oil generated through the UF unit for further packaging.

In order to be reused as cutting oil, the filtrate from this experiment needed to have the following properties: clear with slight yellow color, viscosity < 30 g/cm/sec, pH 6–8, solid content < 0.03%. The operating cycle and service life of the UF membrane was decided based on the turbidity and solid content of the filtrate, which was also used to decide whether the filtration membrane has leakage.

3. Results and Discussion

This experiment was conducted at operating temper-

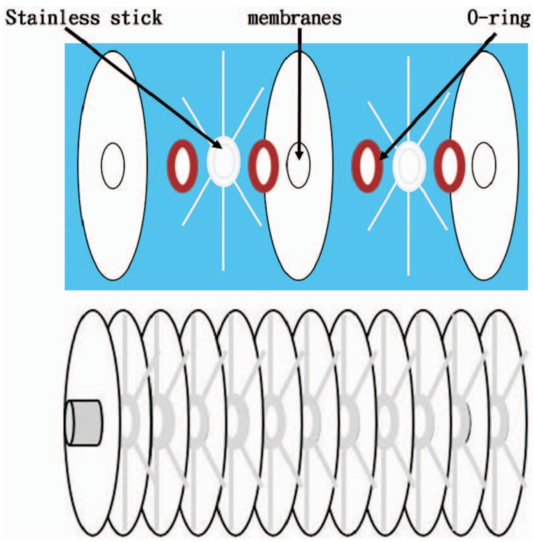

Figure 2. Interior schematic of the UF membrane module.

ature of 60 °C and an operation cycle of 240 hours to ensure the feasibility of commercialization. The results of this study are presented and discussed as follows.

3.1 Energy Consumption

The energy consumption depended on the operation pressure which was also related to the distance of liquid pass through. The cutting oil recycling pathway was the radius of circulate-plate UF membrane (only 9.25 cm) in this experiment (refer to Figure 3). The pressure could be kept below -50.6 kPa while recycling DEG. The energy consumption was only US$ 0.2/kg cutting oil (as electricity). But the energy consumption for other type membranes were 2~10 times because of the operation pressure (over 100.1 kPa).

3.2 Weight Analysis of Materials during Filtration Treatment Process

Weight analysis was conducted based on an one-ton batches of SiC and DEG mixed solution. The weight variation for DEG, SiC and Si by electronic balance were recorded during each stage, including original oil, feed solution, after primary filtration filtrate, and after UF filtrate, are presented in Table 1. The recyclable materials can be recovered 77.3%, which includes 595 kg of SiC and 179 kg of DEG. The recovered cutting oil was brownish in color due to the presence of iron ions. This is caused by iron particles sheared off the surface of the iron wire saw during the slicing process and the iron particles dropped into cutting oil to become ionic state. The aforementioned substances can all be recycled and reused in the manufacturing process. The remaining 228 kg of residual waste after UF can be properly treated by an external waste treatment factory.

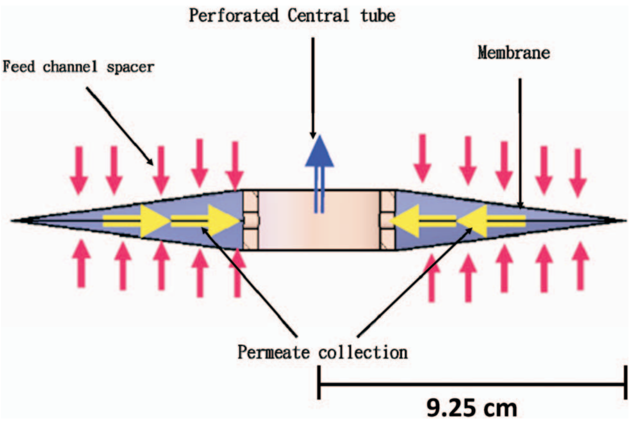

Figure 3. Schematic of flux pathway for recycled DEG.

3.3 Primary Filtration Results

The main purpose of using filter-press equipment for solid-liquid separation is to recover SiC from the spent cutting oil. According to the particle size analysis, the particle size ranged from 0.05 to 50 μm and was averaged at about 9 μm in feeding solution. After primary filtration, the cutting oil still contained a large amount of SiC and Si solids with particle size of less than 5 μm. The solid content of filtrate was much higher than the 0.03%. The filtrate quality could not meet the recycling requirement.

3.4 UF filtration Results

The SiC and Si particles in the primary filtration filtrate could be removed by UF system. Based on the particle size analysis results, the particles ranged from 0.05 μm to 5 μm in size (averaging at 1.3 μm) had been removed by UF system. The recovered cutting oil was transparent. Also, it was about 70% of the original cutting oil used, and had a pH of 6.8, viscosity of 23.1 g/cm/sec, and solid content of less than 0.03%, which meet the reuse requirement for recycled cutting oil. In addition, results of the GC-MASS analysis indicated that recycled cutting oil and new DEG were almost similar in terms of chemical composition (see Figure 4).

Table 1. Weight change of SiC and DEG solution during application and treatment process

Item	Original oil content	Original oil wt%	System feed sol.	Feed sol. wt%	After filter press	After FP wt%	After ultra filtration	After UF wt%
SiC	0.744	74.4	0.744	74.3	0.149	36.6	0.149	65.4
Si	0	0	0.002	0.2	0.002	0.5	0.002	0.9
DEG	0.256	25.6	0.256	25.5	0.256	62.9	0.077	33.7
Total	1.000	100	1.002	100	0.407	100	0.228	100

Note: Based on one ton of initial material.

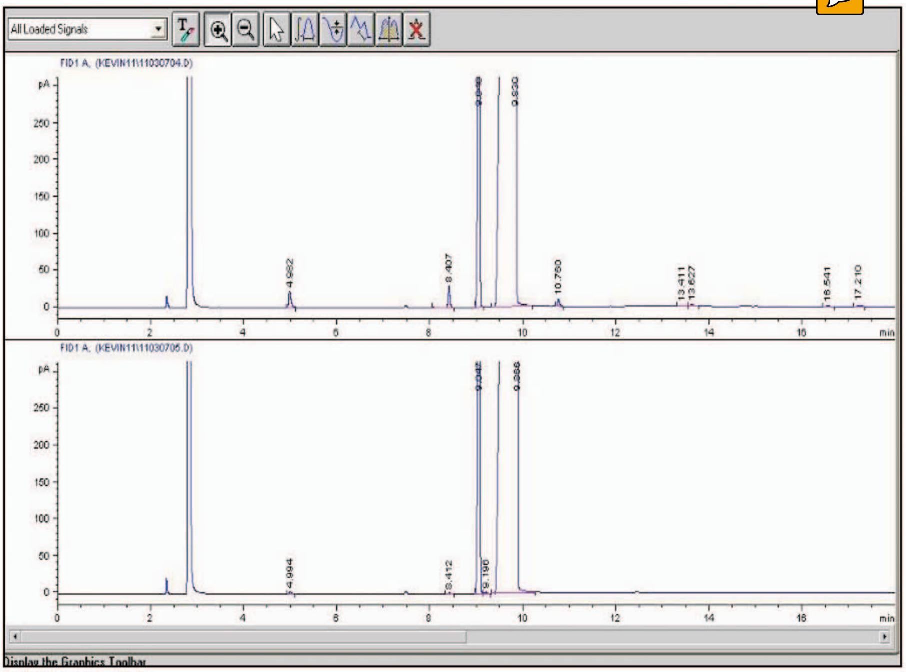

Figure 4. GC-MASS compound analysis comparison between recycle oil (top) and new oil (bottom).

The ICP-AES analysis was conducted to compare the heavy metal content variation between the recovered cutting oil and new DEG. There were 30 items in this analysis. The results indicated that seven substances (Na, Ca, Fe, Mg, Mn, S, and K) has changed because the release and consumed during the cutting process (see Table 2). This results also indicated that there were only a little chemical variation, but the cutting oil operation functions remained the same. The recovered cutting oil was suitable to reuse in the solar cell cutting process.

3.5 Discussion on Characteristics of Blended Recycled Oil and New Oil

After UF, the recovered cutting oil was completely stripped of SiC, Si and Fe, and had less than 0.03% solid content. In order to determine the optimum mixture ratio between recycled and new DEG, the recycled cutting oil was mixed with new DEG in ratios of 100%, 80%, 60%, 40%, 20% and 0%. The pH, viscosity, and conductivity of the mixtures are listed in Table 3. The results showed that the mixture can still comply with the requirements for cutting oil reuse under various blending ratios and the blended oil had slightly higher viscosity but less than 30 g/cm/sec. This is due to the traces of ionic dispersant or defoaming agent present in the used cutting oil which cannot be removed through UF. However, this higher viscosity does not affect the feasibility of reusing the recycled cutting oil. The conductivity decreased as the ratio of recycled cutting increased because of the dilution effect. The conductivity of blended oil was still less than the 100 μS/cm required for reuse.

Also, based on these results and product quality consideration, the optimum blending ratio 60% recycled cutting oil was suggested.

3.6 Cake in the UF Membrane Surface

Changes to the surface of the UF membrane was observed using SEM analysis. There was a compressed cake layer of solids retained by the membrane, and crystallization at the membrane surface was very prominent (as

Table 2. ICP-AES analysis results for recycle oil and new oil (unit: mg/kg)

Sample	Na	Ca	Fe	Mg	Mn	S	K
New oil	115.60	6.05	1.45	1.30	N.D.	216.40	999.10
Recycle oil	218.20	21.34	51.05	17.73	4.77	125.90	790.80

depicted in Figures 5, 6, and 7). The ICP-MS analysis and re-calculation of the oxidized substances at the membrane surface revealed that their composition was SiC and Si (62.47%), DEG and other materials (33.85%), and Fe related compounds (3.48%) (see Table 4). Based on above information, the crystals present at the membrane surface are mainly SiC and Si. These results indicate that there is still a lot of room for future improvement in SiC and Si recovery.

Table 3. Analysis of blended oil characteristics under different blending ratios

Percent recycled oil	pH	Viscosity (cps)	Conductivity (uS/cm)	Viscosity after adding SiC (cps)
0	6.8	23.1	94.6	112
20%	6.5	23.9	89.5	106
40%	6.4	24.2	84.4	106
60%	6.4	24.8	78.9	109
80%	6.4	25.1	72.9	109
100%	6.3	25.7	67.4	111

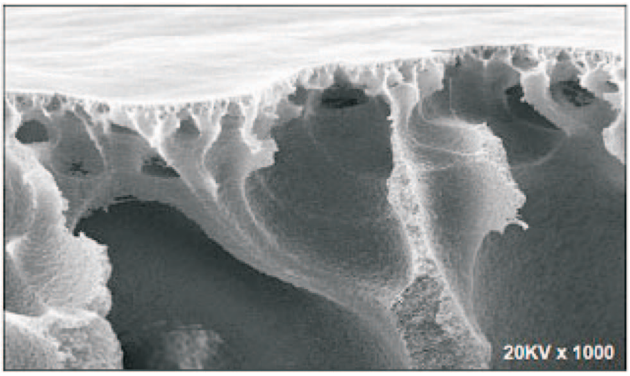

Figure 5. SEM image of the surface of UF membrane prior to filtration.

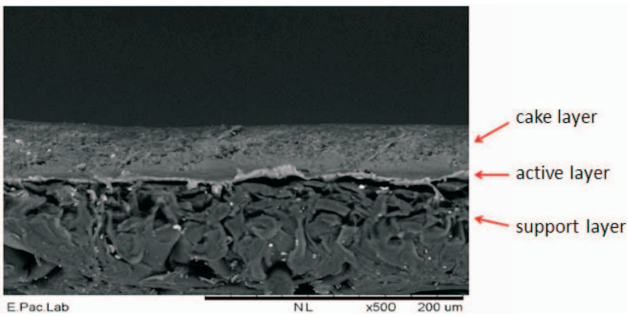

Figure 6. SEM image of the surface of UF membrane after filtration.

3.7 Economic Analysis

A plant with an annual production capacity of 200 MW of solar wafers and monthly production of 4.6 million pieces of wafers uses 5,000 tons of DEG per year. Given that only new DEG is used and that each ton of DEG costs US$ 2,333.34, the plant's annual spending on new DEG will be approximately US$ 11.67 million dollars. Usually, the cost of recycled DEG is 40% off than new DEG in market. If the blending ratio of 60% recycled DEG were implemented, then annual savings in cutting oil could be about US$ 2.8 million dollars. Otherwise, the used cutting oil had to be treated as waste. The typical 200 MW plant will generate 7,950 tons of such waste each year. Based on the disposal cost of US$ 100 for each tons of waste in Taiwan, the total annual cost in managing such waste is about US$ 795,000. This study demonstrates that waste can be reduced by 77.3%, saving US$614,535 in disposal costs per year. Therefore, the to-

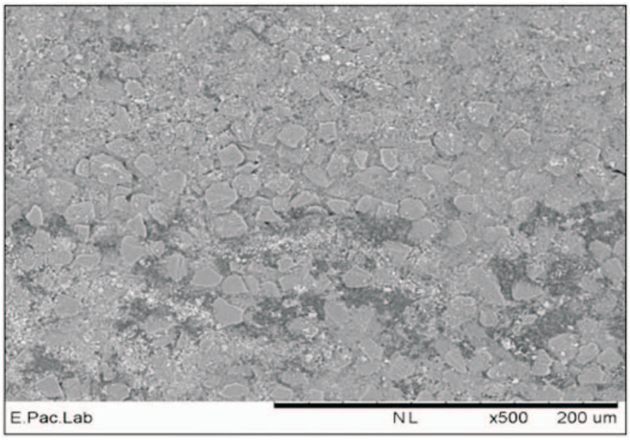

Figure 7. SEM image of the surface of UF membrane after filtration showing accumulation of Si crystals.

Table 4. ICP-MS analysis of residual filtrate

Test item	Test result (wt%)
Si	4.07
SiC	58.40
Al_2O_3	N.D.
Na_2O	0.05
K_2O	0.09
MgO	N.D.
CaO	0.05
TiO_2	0.01
Fe_2O_3	3.48
DEG and others	33.85

tal annual savings for manufacturing 200 MW PV can be about US$ 3.414 million dollars, with a saving rate of 27.4%.

3.8 Comparison the Cutting Oil Recovery Method with UF Filtration and Distillation

The traditional cutting oil recovery used the distillation [13−15]. This method also is popular process in chemical engineering. The UF membrane filtration is the alternative method to recover the cutting oil. The UF membrane filtration has several advantages as follow:

1. The total capital investment and operation cost of UF membrane filtration were lower than distillation.
2. The energy consumption of UF membrane filtration (US$ 0.2/kg as electricity) was lower than distillation (US$ 1.0/kg as electricity).
3. Although the degree of purity of filtration cutting oil (above 95%) was lower than distillation (almost 100%), the percentage of reuse of filtration cutting oil (50~60%) was higher than distillation (below 35%).
4. The manufacture cost of filtration cutting oil (US$ 1.4/kg) was lower than distillation (US$ 2.45/kg).
5. The filtration can work inside the factory except distillation.

4. Conclusions

The rotational UF system is suitable and effective process for recycle cutting oil from highly viscosity waste in solar photovoltaic cell manufacture. In this study, the adoption of a rotating circular plate UF membrane resulted in 70% recovery of used cutting oil. The recycled cutting oil can be blended with new DEG at an optimum blending ratio of 60%, thus reducing manufacturing costs of wafer slicing by over 27.4%, and recycling over 77.2% waste. This clean technology also considered the physical and negative pressure operational conditions that can save energy about 50%. The final 22.8% residual waste also still can be purified and recovered by other new technologies as reference. The clean process will be fully reached.

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