



Application of KOH-ethanol Solution in Separation of Waste Photovoltaic Panels

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ABSTRACT

With the continuous development of photovoltaic panel technology in recent years, the frequency of replacement has accelerated, which has led to the continuous increase of waste photovoltaic panels. Developing the separation technology of waste photovoltaic panels can effectively solve the problems of resource shortage and environmental pollution. According to the sticking mechanism of EVA film, this paper proposes a KOH-ethanol solution to degrade EVA film and recover silicon from waste photovoltaic panels. In this paper, the key factors affecting the separation of photovoltaic panels are studied through experiments indicating that compared with NaOH-ethanol solution, KOH-ethanol solution has better separation efficiency. Sample after crushing treatment has higher separation efficiency, the best temperature for sample separation is 200 degrees Celsius, and the best sample area is 1×1 square centimeter, the optimal concentration of the solution is 0.20 mol/L, and the optimal reaction time is 3.0 hours.

INTRODUCTION

As the global population continues to increase, our demand for new energy will increase, and the resulting environmental pollution problems will become more prominent. Research and analysis point out that in the next 60 years, the existing fossil fuels on the earth will be at risk of being depleted (Li et al. 2018). The CO₂, SO_x, NO_x and other pollutants generated in the process of fossil resource consumption will cause acid rain and greenhouse effect, which will seriously pollute water, soil and air. At the same time, the reserves of fossil resources are relatively limited, and the difficulty and cost of mining continue to increase. Therefore, in terms of energy supply, it is necessary to follow the path of sustainable development and vigorously develop new types of high-efficiency, clean and renewable energy sources, which has become a common consensus of all countries in the world. With the continuous advancement of current technology, people have begun to regard solar energy as an important part of new energy, and develop a variety of new technologies to replace fossil fuels. As an emerging renewable energy, solar energy has the following advantages: (1) Energy can be used for a long time; (2) Abundant reserves; (3) High safety; (4) Low cost; (5) Clean energy has relatively small impact on the environment. Therefore, solar energy has always been considered to have broad development prospects (Yan et al. 2012).

The life span of photovoltaic panels is 25-30 years (Ma et al. 2021). Due to the long service life, waste photovoltaic panels have been ignored by humans. However, according to

related reports, photovoltaic panels have been installed from the earliest 80s to 90s, and in recent years there have been photovoltaic panels that have reached their lifespan (Aflaki et al. 2021). In addition, due to the replacement of photovoltaic technology, the reduction of photoelectric conversion rate, the damage of photovoltaic equipment, the aging of photovoltaic modules, etc., the growth of waste photovoltaic panels has been further accelerated and has attracted widespread attention (Paiano 2015). According to statistics, the global photovoltaic waste volume reached 43,500 to 25 million tons in 2016. It is estimated that the world will reach 1.7-8 million tons in 2030, and the global photovoltaic waste will reach 0.6-78 million tons in 2050. Among them, there will be about 500 tons of waste photovoltaic panels in China in 2020. It is estimated that China will reach 20 million tons in 2050, which is equivalent to 2000 times the weight of the Eiffel Tower. Based on the above data analysis, there will be a large number of waste photovoltaic panels in the world that need to be processed in the future (Hu 2008, Farrell et al. 2019, Tian et al. 2021, Maranghi et al. 2019).

In order to cope with the substantial growth of photovoltaic cell waste in the future, it is of great significance to study the multi-component high-efficiency separation technology of photovoltaic panels.

Due to the large reserves of silicon and easy exploitation, silicon-based photovoltaic panels account for 90% of the entire photovoltaic market. The remaining 10% photovoltaic panels mainly include copper, indium, gallium, selenium,

amorphous silicon and cadmium telluride (Stephanie et al. 2016, Xu et al. 2018, Azeumo et al. 2019). Therefore, this research focuses on the recycling of silicon-based photovoltaic panels.

Traditional silicon-based photovoltaic panels are single-layer glass crystalline silicon solar panels (single-glass photovoltaic cells). Single-glass photovoltaic cells mainly include toughened glass, polyethylene-vinyl acetate copolymer (EVA) film, silicon-based solar cells, polyvinyl fluoride composite (TPT) backplanes, metal electrodes, aluminum frames, and connectors. Among them, the aluminum frame plays the role of protecting the solar panels and fixing connections, and can be directly recycled by mechanical or manual removal. Photovoltaic panels are generally placed outdoors for a long time. In order to protect photovoltaic panels from external moisture and external forces, tempered glass and TPT backplanes play a role in protecting silicon-based solar cells. At present, the most widely used adhesive for photovoltaic panels is EVA adhesive film, which has the advantage of low cost, good performance, and stable chemical properties. The main component of the TPT backsheet is a polyvinyl fluoride composite film, which consists of two parts, namely ethylene phthalate and polyvinyl fluoride. Its function is to seal, insulate, waterproof, and resist aging. The connector is to protect the normal operation of the entire power generation system.

In traditional chemical separation, organic chemical swelling agents (such as toluene and trichloroethylene) are used to dissolve the EVA film in the photovoltaic panel to achieve complete separation of photovoltaic cells. However, organic chemical swelling agents usually have greater volatility and toxicity which does not meet the green, environmental, and sustainable recycling goals.

In this paper, based on the sticking mechanism of EVA film, the structure of EVA and the characteristics of the interface of each component are destroyed by chemical reagents, and a new chemical reagent KOH-ethanol is developed to realize the separation of the components of photovoltaic cells. This chemical reagent has the characteristics of low toxicity and recyclability, and has the characteristics of low energy consumption compared with the high-temperature heat treatment separation method. Therefore, using this method of recycling, photovoltaic panels can effectively protect the environment and carry out secondary use of resources.

This work carried out a detailed experimental study on the separation mechanism of KOH-ethanol on photovoltaic panel modules, focusing on the influence of size, alkali type, experimental temperature, KOH concentration and the solid-liquid ratio of the material on the separation rate of photovoltaic panels.

BASIC THEORY

As an adhesive, EVA is the most commonly used material for bonding the components of photovoltaic panels and protecting photovoltaic panels from external moisture and mechanical damage. It is generally believed that the most important step in the recycling process of photovoltaic panels is the removal of EVA. Therefore, this article focuses on the adhesion theory of EVA.

Since EVA is a weakly polar substance, it has weak adhesion to glass and TP backplanes. Generally, a coupling agent is added to increase the viscosity during the EVA cross-linking process. The commonly used coupling agent is a silane coupling agent, the chemical formula of is SiRX_3 . Its R is an organophilic group, which can chemically react with EVA, such as amino, vinyl, epoxy, methacryloxy and so on. X is an inorganic group, which can react chemically with the surface of an inorganic substance, such as an alkoxy group. The adhesion mechanism of EVA and photovoltaic panels are shown in Fig. 1.

Through the analysis of the adhesion theory, the adhesion of each component of the photovoltaic panel is mainly connected by chemical bonds. The different components are bonded together through the action of chemical bonds. EVA forms a gel with a three-dimensional network structure during the cross-linking process, and the coupling agent plays a role in enhancing the adhesion of EVA.

In the process of separating the components of the photovoltaic panel, it is first necessary to ensure that the chemical test reagent can effectively penetrate the middle layer of the photovoltaic panel and can immediately react with the EVA film. For example, the use of high-frequency vibration in ultrasonic radiation technology can effectively promote the diffusion process of chemical reagents in the middle layer of the photovoltaic panel, and at the same time can effectively accelerate the dissolution rate of EVA. In addition, the use of alkaline solution such as NaOH or KOH can also promote the reaction between it and the anti-reflective coating, thereby separating other layers including aluminum and silicon.

MATERIALS AND METHODS

Experimental Materials and Reagents

Experimental raw materials: Waste silicon-based photovoltaic panels and crushed materials.

The main reagents of the experiment: KOH, NaOH, absolute ethanol, deionized water (conductivity $<0.1 \mu\text{S}/\text{cm}$, derived from CM-230 deionized water).

Laboratory Equipment

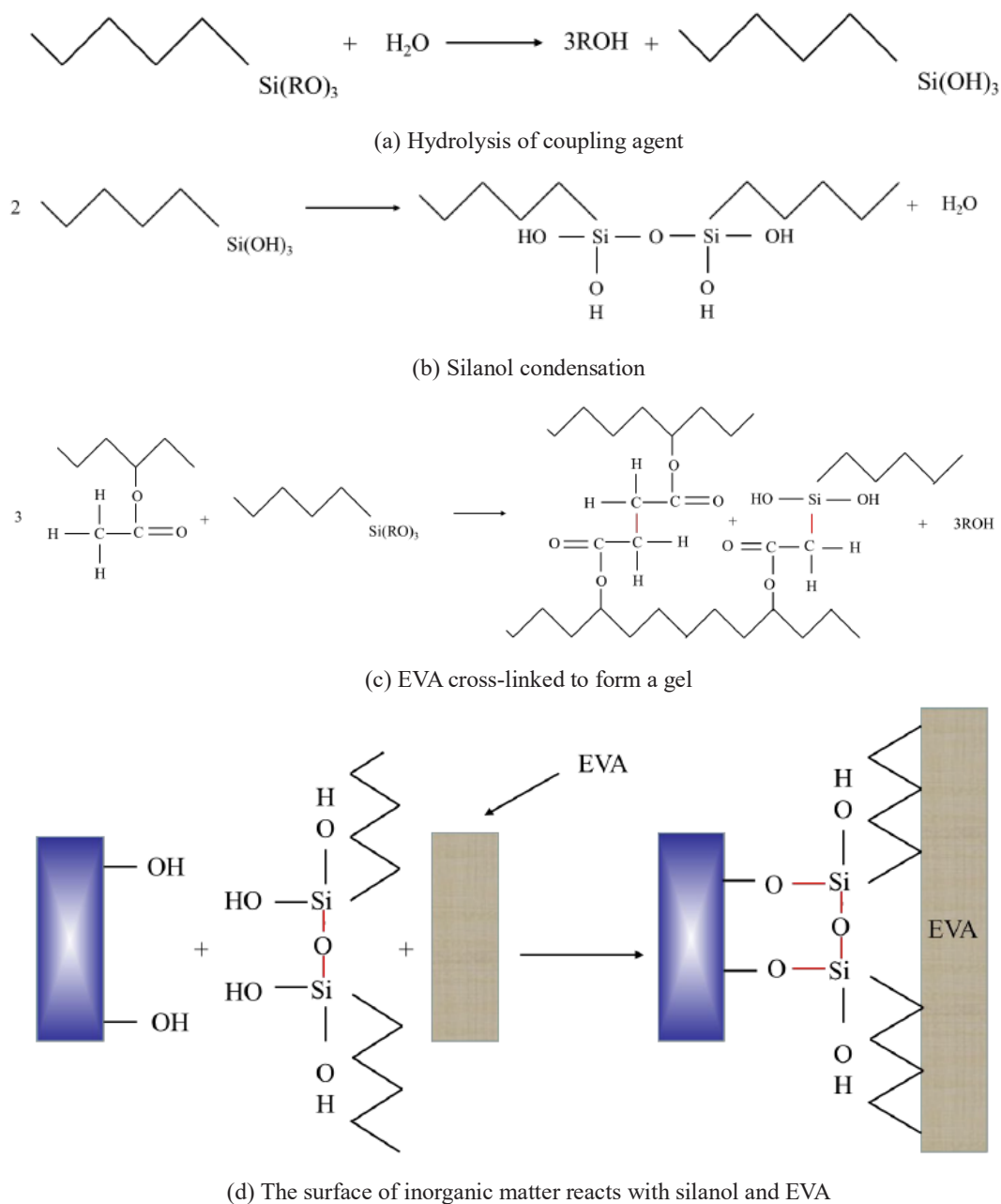


Fig. 1: The adhesion mechanism of EVA and photovoltaic panels.

Main experimental equipment: As shown in Fig. 2, using KSS-1350° type muffle, the temperature of the reactor is controlled by a programmable temperature controller with an accuracy of $\pm 2^\circ$. DF-1015 type heat-collecting magnetic heating stirrer.

Other equipment: SHB-III type circulating water multi-purpose vacuum pump. One PG-2D metallographic polishing

machine. One ZK-1BS electric heating vacuum drying oven. Hydrothermal reactor, 1 condensation recovery device. BS-224S electronic balance, precision 0.0001 g.

Analysis Test Method

The weighing method is used to calculate the separation rate of photovoltaic panels by weighing the mass before



Fig. 2: Picture of Muffle furnace

and after the separation with an electronic balance (Formula 1).

$$\text{Separation ratio (\%)} = \left(1 - \frac{G_b}{G_a}\right) \times 100 \quad \dots(1)$$

In the above formula, G_a represents the total mass of photovoltaic panels, and G_b represents the mass of unseparated photovoltaic panels.

Since silicon-based cells have cathodes and anodes, an oxide layer will be generated on the surface of the silicon wafers during the process of separating photovoltaic panels using high-temperature heat treatment or alkali-ethanol solvents. In order to study the influence characteristics of wafer recovery rate under different separation methods, after the photovoltaic panels are completely separated by different treatment methods, the recovery rate of the silicon wafers was computed using the Formula 2.

$$W_{q1} (\%) = \left(1 - \frac{W_{b1}}{W_{a1}}\right) \times 100 \quad \dots(2)$$

In the above formula, the recovery rate of the silicon wafer is represented by W_{q1} , the thickness of the oxide layer is represented by W_{b1} , and the thickness of the silicon

wafer is represented by W_{a1} . There is a close relationship between the degree of oxidation of the silicon wafer and its recovery rate.

1) Detection of the Oxidation Degree of the Surface

Experimental test method: X-ray photoelectron spectrometer was used to measure the valence state of the silicon wafer surface.

2) Scanning Electron Microscope Analysis (SEM)

Experimental test method: The morphology of the silicon-based cell was obtained by the JSM-7800 scanning electron microscope detecting high temperature heat treatment, KOH ethanol and NaOH-ethanol separation. The thickness of EVA film before and after the KOH-ethanol treatment was measured.

3) Measurement of Silicon Oxide Layer Thickness

Experimental test method: The wavelength or intensity of the characteristic X-rays generated by an energy spectrometer (EDS) was measured, so as to quantitatively analyze the oxide layer thickness of silicon wafers by measuring the wavelength of silicon and oxygen in the measurement area.

4) Contact Angle Measurement

Experimental test method: Use DSA100 contact angle measuring instrument, and high-speed camera to record the wetting process of water and ethanol droplets on the glass respectively; intercept the image at the time when the drop is stable, take the picture; and use the five-point method to automatically fit the circle to calculate contact angle.

5) Roughness Measurement

Experimental test method: The Nano GT-K optical profiler provided by the German Bruker Company was used. The roughness of the glass obtained by high-temperature heat treatment, KOH ethanol and NaOH-ethanol separation was carried out respectively.

6) Fourier Infrared Test and Analysis (FTIR)

Experimental test method: The original swelling agent, the post-reaction swelling agent, and the EVA film before and after swelling were analyzed by T-27 Fourier infrared spectroscopy provided by the German Bruker Company. The infrared spectrum was recorded in the transmission mode, and the recording range was between $7.0E+02$ and $4.0E+03 \text{ cm}^{-1}$. The manual sampling method was used to sample the EVA film of the photovoltaic panel, and the ATR attenuated total reflection was used. The method scans the film sample. In the process of preparing the solution sample, the ethanol

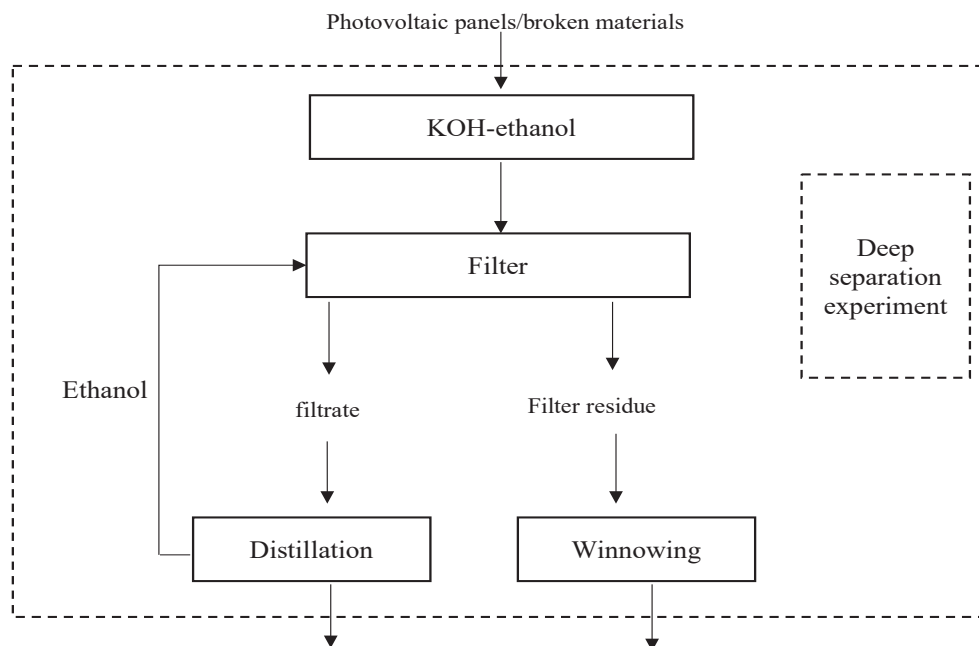


Fig. 3: Flow chart of deep separation of photovoltaic panels by chemical method.

in the solution was removed through the evaporation process, thereby reducing its influence on the measurement results.

Experimental Steps

The experimental steps are shown in Fig. 3.

- (1) Cut the waste photovoltaic panels into 1×1 , 2×2 and 3×3 cm^2 and mechanically crush the pretreated materials.
- (2) The photovoltaic panel was crushed into fragments, and at the same time, 200 mL of alkali-ethanol solution was used to soak, and the solution was heated in a muffle furnace to control the reaction temperature.
- (3) After the reaction, the solution was suction filtered, the filter residue was thoroughly washed and dried at 130°C for 12 h. Winnowing was used to obtain silicon wafers and glass.
- (4) The filtrate was distilled, the remaining KOH crystallizes out, and the ethanol solution was recycled.

RESULTS AND DISCUSSION

Study on the Variation of Separation Rate in Different Alkali Types

In order to study the relationship between the separation rate of photovoltaic panels and the KOH-ethanol or NaOH-ethanol solution, and to determine the effect of different alkali types on the separation rate, experimental methods were used to carry out the research. The experimental temperature was 200 degrees Celsius, the alkali concentration was 0.21

mol/L, and the area of the photovoltaic panel was 1×1 cm^2 . As shown in Fig. 4, the separation speed in KOH-ethanol was higher than that in NaOH-ethanol solution. The former requires 3.1 hours to complete the separation, while the latter requires 4.1 hours to complete the separation. The conclusions of this research show that the separation rate of photovoltaic panels in KOH-ethanol increases faster than that of NaOH-ethanol. Therefore, due to its better separation effect, the subsequent experiments used KOH-ethanol solution as the reaction reagent.

Photovoltaic Panel Size and Effect of Temperature on Separation Rate

This paper studies the effect of photovoltaic panel size on its

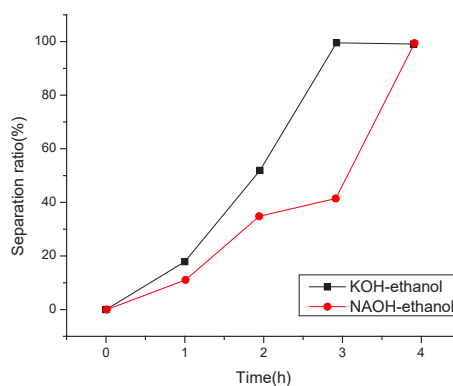


Fig. 4: Variation curve of separation rate in different solutions.

separation rate. The research conclusion shows that when the size of the photovoltaic panel is 1×1 square centimeter, the separation rate increases rapidly, and the entire separation can be completed within 3 hours. However, when the size is 2×2 square centimeters, the entire separation process cannot be completed within 3 hours. When the size is 3×3 square centimeters, the separation rate is very slow. At 3 hours, the separation rate is only 65%. Therefore, a photovoltaic panel of 1×1 square centimeter can obtain the highest separation rate.

This paper studied the effect of using KOH-ethanol solution for the separation of waste photovoltaic panels when the temperature is between 160-200°C, the solution concentration of KOH is 0.2 mol/L KOH, the solid-to-liquid ratio is 55 g/L, and the size of the photovoltaic panel is 1×1 square centimeter. The research conclusion shows that at 160°C, 43% of the photovoltaic panels can be separated in 6 hours, the separation rate shows an increasing trend between 1-3 hours. At 180°C, 75% of the photovoltaic panels can be separated in 6 hours. At 200°C, it only takes 3 hours to complete the separation of the entire photovoltaic panel. Therefore, considering the separation effect of photovoltaic panels, the optimal reaction temperature and reaction time can be set at 200°C and 3 h.

The Effect of Alkali Concentration on Separation Rate

During the study, the concentration of the KOH solution was 0.10-0.30 mol/L, the temperature of the experiment was 200 degrees Celsius, and the duration of the experiment was 2.51 h. The solid-to-liquid ratio in the solution is 54 g/L, and the area of the sample is 1×1 square centimeters. As shown in Fig. 5, the separation rate increases with the increase of the solution concentration. During the process of increasing the solution concentration from 0.10 to 0.20 mol/L, the increase in the separation rate is larger, and at 0.2-0.3 mol/L. In the

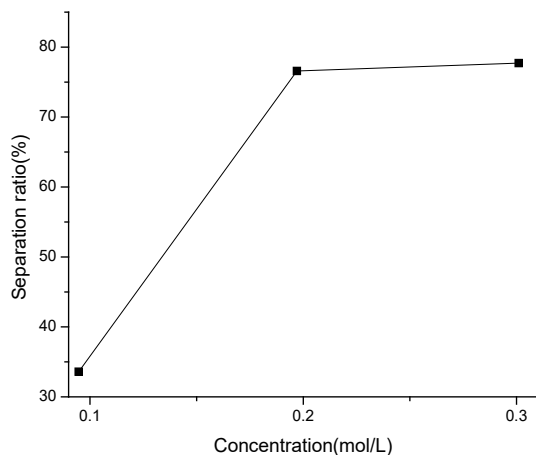


Fig. 5: Change curve of solution concentration and separation rate.

solution concentration range of, the increase in separation rate does not change significantly, so the optimal solution concentration value is 0.2 mol/L.

Mechanical Crushing Strengthens Chemical Separation

In order to explore the impact of mechanical crushing pretreatment on the separation of waste photovoltaic panels, the experiments were carried out in KOH-ethanol solution with unbroken photovoltaic cells and crushed materials of one size. The area of the sample is 1×1 square centimeter, the experimental temperature is 200 degrees Celsius, the solution concentration is 0.20 mol/L, and the solution concentration is 55.0 g/L. As shown in Fig. 6, the separation rate of photovoltaic cells is closely related to the degree of fragmentation. After the sample is broken, the separation rate reaches 58.0%. When the reaction reaches 2 h, the separation rate is 58%. However, when the raw material is a photovoltaic panel that has not been mechanically broken, even if the reaction time is 2 h, the separation rate is only 42%. In order to achieve complete separation of photovoltaic panels, the reaction time needs to be extended to 3 h. Therefore, according to the above experiments, the mechanical crushing treatment greatly shortens the separation time of photovoltaic panels and improves the recycling efficiency.

The Influence of Different Media on the Separation Rate

In order to study the influence of different media on the separation of photovoltaic panels, after the mechanical crushing pretreatment, KOH-water solution and KOH-ethanol solution were used for experiments. The experimental temperature is 200 degrees Celsius, the solution concentration is 0.20 mol/L, and the solid content is 55.0 g/L. The results are shown in Fig. 7. It can be seen that the KOH-ethanol solution system is better than the KOH-water system. Using KOH-ethanol solution, the photovoltaic panels can be completely separated

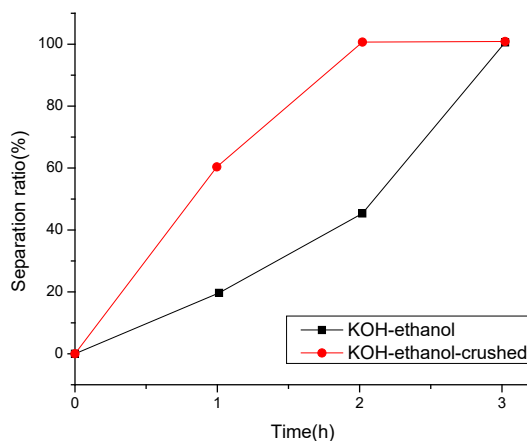


Fig. 6: Change curve of separation rate of crushed sample.

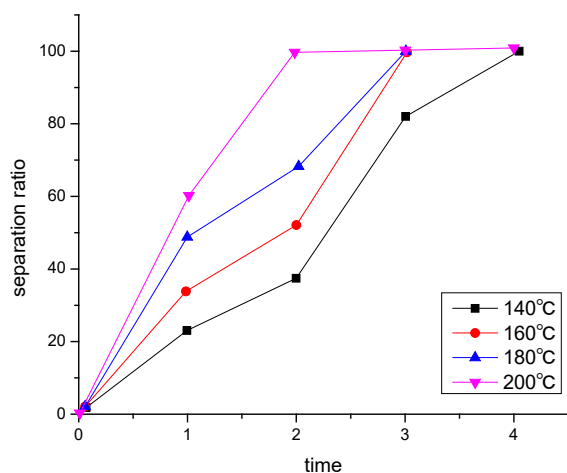


Fig. 7: Variation curve of separation rate under different media.

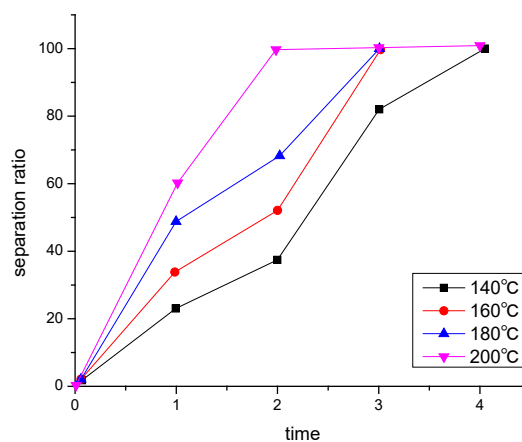


Fig. 8: Variation curve of separation rate of broken samples at different temperatures.

after only 2 hours of reaction. When using the KOH-water system to react from 1 h to 2 h, the separation rate of photovoltaic panels increased from 8% to 22%. Although the reaction time was increased to 3 hours, the separation rate of photovoltaic panels was only 38%. Therefore, the follow-up experiment uses the KOH-ethanol system to separate photovoltaic panels.

Effect of Reaction Temperature on Separation Rate After Mechanical Crushing

In order to discuss the influence of the reaction temperature on the separation of photovoltaic panels, the experimental temperature was separately discussed (140-200°C) for 2 h. The concentration of the solution is 0.20 mol/L, and the solid-to-liquid ratio in the solution is 55.0 g/L. As shown in Fig. 8, when the reaction temperature rose from 140°C to 200°C, it was found that the separation rate of photovoltaic panels increased significantly. When the reaction temperature is 140°C, the separation rate increases slowly compared with other experimental temperatures. When the reaction temperature increases to 160°C, it takes 4 h for the photovoltaic panels to completely separate. When the reaction temperature is 180°C and the reaction is carried out for 2 hours, the separation rate of the photovoltaic panels is 63%, and the complete separation requires 3 hours of reaction. However, when the reaction temperature is 200°C, the separation rate of the photovoltaic panels increases rapidly, and the complete separation only takes 2 h. Therefore, the subsequent experiment uses 200°C, and the reaction temperature time is 2 h.

Medium Circulation

The use of KOH-ethanol solution to separate photovoltaic panels requires a large amount of ethanol solution. Therefore, from the perspective of green, environmentally friendly and sustainable recycling, it is necessary to consider the

recycling and utilization of waste liquid. In the experiment, the separated solution was distilled for 0.5 h at a reaction temperature of 130°C. The distilled solution was analyzed by FT-IR, and the solution recovered has the same structure as the original solution. Therefore, the waste liquid can be recycled and reused by distillation.

CONCLUSION

This paper has developed an environmentally friendly, efficient, and closed-loop recycling process. Compared with NaOH-ethanol solution, KOH-ethanol solution has better separation efficiency. The sample after crushing treatment has higher separation efficiency. The best temperature for sample separation is 200 degrees Celsius, and the best sample area is 1×1 square centimeter, the optimal concentration of the solution is 0.20 mol/L, and the optimal reaction time is 3.0 hours. Compared with water, ethanol is more suitable as a solvent for separation of photovoltaic panels. Ethanol solvent can make sample components enter the inner layer of photovoltaic panels faster, thereby effectively separating specific components in the sample. The research results of this article have broad application prospects in engineering projects.

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