2 Role of Process Simulation in Extraction Technologies for Medicinal and Aromatic Plants

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Abstract

This paper illustrates the role of process simulation in the field of extraction technologies for medicinal and aromatic plants. The paper starts with a brief introduction to process simulation fundamentals and the role of process simulation in the industry today. It describes procedures to follow in simulating a process and the benefits of process simulation. In the second part of the paper, phytochemical processes that have been simulated at ICS-UNIDO are listed, followed by two case studies to illustrate the applicability of the methodology proposed: (i) turpentine oil batch distillation and (ii) menthol recovery by crystallization of mentha oil. At the end, recommendations are given advocating the importance of process simulation for developing countries.

2.1 Introduction

Developing countries are rich in medicinal and aromatic plants (MAPs) but, due to difficulty in accessing efficient extraction technologies, value addition to this rich bioresource is difficult. In most cases, and particularly in very poor countries, the technologies used are inappropriate and not economical. The crucial problem is related to the quality of the product: primitive extraction technologies do not guarantee a stable and high-quality product and, in some cases, inappropriate technologies and procedures result in producing contaminated product which has low market value.

In order to assist developing countries to achieve the objective of using rich MAP resource for producing value-added products, dissemination of knowledge of existing extraction technologies and of the latest developments in these technologies is essential.

Commercial process simulation software can be used to predict, on a computer, the real plant and consequently is a useful tool for optimizing the process conditions and enhancing the capacity of managing the phytochemical processes. In particular, process simulation can assist developing and emerging countries in optimizing an advanced process rather than managing a primitive process, which should be substituted by more efficient and standardized procedures. The focus in this case is more related to practical problems such as the quality of the materials and of the water to be used for the extraction. In most cases, developing countries face problems in the type of vessel, quality of water and stability of the product during the processing.

This paper describes the use of process simulation software in the extraction and purification of essential oils at both pilot and industrial scales. Such processes have been developed and are in operation in developing and emerging countries. The goal of this paper is to illustrate a procedure for obtaining better knowledge of the extraction process and, therefore, for optimizing the process in terms of energy use, raw material consumption and environmental impact.

2.2 Process Simulation Goals and Definitions

Simulation is the act of representing some aspects of the real world by numbers or symbols which may be manipulated to facilitate their study. A process simulator is an engineering tool that performs several tasks, including automated calculations, material and energy balances, physical property estimations, design or rating calculations, and process optimization. A process simulator is not a process engineer, and a process engineer is always needed to analyze the problem and the output of a process simulator. A process simulator solves material and energy balances by means of computer code.

In principle, a process simulator for the study of a chemical process goes through the procedure outlined in Figure 1. One starts from the definition of the problem (problem analysis) and then develops the process model, i.e. the system of equations (algebraic or differential). Furthermore, one collects the necessary additional data and solves the model with a suitable method, depending on the system of equations. Finally, the process engineer analyzes the results and perhaps starts over again to develop a more realistic model.

The same picture applies to steady-state simulation, dynamic simulation and optimization problems; only the process model and the method of solution change. Solution of the system of material and energy balance equations is not an easy task because it must be solved considering many components, complex thermophysical models for phase equilibrium calculations, a large number of subsystems (equipment), rather complex equipment (e.g. distillation columns), recycle streams and control loops.

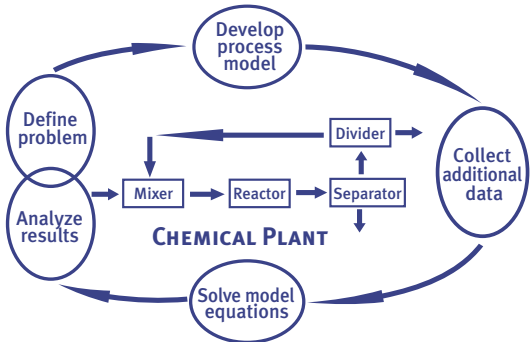


Figure 1: Fundamental steps in running process simulation software

A typical process simulation scheme, with the most important elements and their connections, is shown in Figure 2. Clearly, a process simulator includes cost estimation as well as economic evaluation. The importance of the database is shown in the figure as a necessary source of information for different objects in the structure.

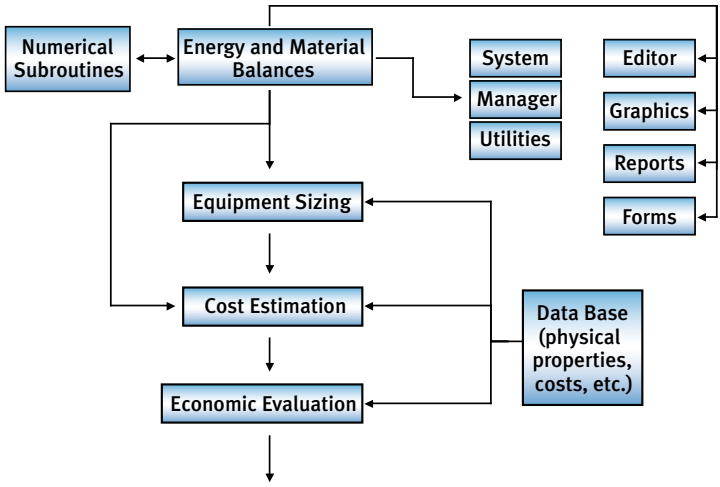


Figure 2: General scheme of a steady-state process simulator

The following approaches are available in process simulation:

- Steady state simulation, which considers a snapshot in time of the process.
- Dynamic simulation, which considers the evolution in the time domain of the equations describing the process.
- Integrated steady-state–dynamic simulation, which combines the previous two approaches.

These three approaches may be used in different ways when dealing with process simulation. One possibility is to perform *process analysis*, in which an existing process is studied and alternative conditions as well as dynamic behavior are investigated in the appraisal of effectiveness of the design. The second is *process synthesis*, in which different process configurations are compared in order to identify the best choice of units and the connections between them. The third possibility is *process design and simulation*, which aims at establishing the optimal operating conditions of a given process.

In all these possibilities, impact on industry is pervasive rather than restricted to a single moment in the development of the process. Process simulation has strongly affected the way engineering knowledge is used in processes. The traditional way of using process simulation was mainly focused on designing flowsheets and on defining critical equipment parameters, such as distillation column stages and column diameter. Today,

engineers are oriented to a more comprehensive use of process simulation in the entire "life" of the plant, as in designing control strategies, optimizing process parameters, studying process time evolution for understanding startup and shutdown procedures, performing risk analysis, training operators, and defining procedures to reduce non-steady-state operations.

The main benefits gained from such a comprehensive use of process simulation are the partial or total replacement of pilot plants (reduction of the number of runs and planning), the reduction of time to market for the development of new processes, and the fast screening of process alternatives to select the best solution in terms of economics, environmental aspects, energy consumption and flexibility. Due to the high complexity of chemical processes, to get these benefits one must critically simplify the process and apply process simulation techniques in the entire life cycle of a process.

Steady-state simulators are considered the core products of process simulation and are used for designing processes, evaluating process changes and analyzing what-if scenarios. Steady-state simulation is normally performed before all other kinds of simulation: dynamic simulation, process synthesis with pinch technology, detailed equipment design, off-line and on-line equation-based optimization, and application technologies for vertical markets (e.g. polymers).

The problems involved in a process simulation run are the definition of an accurate thermodynamic model (equations of state or excess Gibbs energy model), the necessity of defining dummy operations (not always easy to identify), and the tear streams identification to achieve rapid convergence.

The logical procedure for performing a simulation is as follows. First, one defines all the components to be used in the simulation, including conventional and non-conventional components. Next, the most important step in the definition of the simulation is the selection of physicochemical properties to be used in the calculations. Having done this, one proceeds to flowsheet connectivity and to the definition of the feed conditions. The next step is the unit operation internal definitions. At this stage, it is possible to run a base case and check that the system is converging.

Process specification definition, control parameters, and equipment hold-up definition are added later to refine the simulation and to obtain results similar to the reality. Various different results are obtained from a simulation run. The most important are the validation of phase equilibria models for the real system to be used in similar conditions, the verification of the process operating conditions, information on intermediate streams and enthalpy balance, verification of plant specifications, and influence of the operative parameters on the process specifications.

All this information is useful for de-bottlenecking the entire process, or part of it, for identifying process control strategies, and for tuning the instrumentation. This is important since it allows one to verify the behavior of security systems when process conditions are varied.

As far as dynamic simulation is concerned, applications can be found in continuous processes, concurrent process and control design, evaluation of alternative control strategies, troubleshooting process operability, and verification of process safety.

The most important benefits of dynamic modeling are: the capital avoidance and lower operating costs through better engineering decisions; the throughput, product quality, safety and environmental improvements through improved process understanding; and the increased productivity through enhanced integration of engineering work processes.

2.3 Biotechnological and Phytochemical Processes Studied at ICS-UNIDO

This section summarizes ongoing work involving the simulation of important biotechnological and phytochemical processes.

2.3.1 Brief of Biotechnological Processes

2.3.1.1 Alcohol Production from Biomass

The goal of the process is the steady-state simulation of the production of ethanol from biomass fermentation. The process is divided into two parts: (i) biomass fermentation that produces a mixture of ethanol, water and other components, and (ii) separation using a distillation column that concentrates the ethanol. The modelled reactors are continuous stirred tank reactors in series or parallel.

2.3.1.2 Soybean Oil Refining and Treatment of the Waste

The goal of this work is to simulate the soybean oil refining process. This is a complex biotechnological process that involves many reactions and the treatment of solids. The process is divided into three sections: (i) degumming and neutralization, (ii) bleaching, and (iii) deodorization. The main objective of the simulation is to reduce the consumption of steam by applying the pinch technology concept. Steam is consumed in the heat exchangers to heat the oil, in the bleacher equipment, and in the deodorizer. The difficulty of this simulation lies in the large number of undefined components that must be characterized in order to obtain a reliable simulation. In addition, an alternative way of reducing the free acids, by using extraction

with ethanol, is being examined. Key features are the achievements of the required product quality by minimizing the capital and operating costs.

2.3.1.3 Production of Synthetic Hydrocarbon Fuels from Biomass

Starting from natural gas, coal, or wood, a syngas of suitable composition can be produced by gasification. Then, water-gas shift reaction, Fischer-tropsch synthesis and hydrocracking can be applied to the syngas to obtain a mixture of liquid hydrocarbons that can be used as synthetic fuel. This is a complex process that can be simplified by neglecting the kinetics of the chemical reactions involved. The purpose of this project is to quantify the mass and energy consumption and the emission of carbon dioxide. Key features are: the selection of the thermodynamic model to achieve a realistic simulation; the heat integration among different process sections to minimize the environmental impact during recovery and recycling of the entrainer; and the reduction of energy duties.

2.3.1.4 Production of Bio-ethanol from Corn

By fermentation of sugar cane, corn or wheat, ethanol (bio-ethanol) can be easily produced. This process includes the steps of liquefaction, cooking, fermentation, distillation, dehydration, evaporation and drying of the solid by-product. By a careful simulation of the operations involved, the needs for water and energy can be minimized, and the use of fossil fuels can be avoided. Key features are the energy balance starting from the content in the feedstock biomass, and the water saving.

A second problem can be addressed by accurately simulating the distillation and dehydration aspects, which have the highest energy demand of this process. Key feature is the use of pressure as an operating variable.

2.3.2 Brief of Phytochemical Processes

2.3.2.1 Citral Recovery by Distillation of Lemon Peel Oil

The goal of this process is the production of citral. Lemon peel oil is fractioned by a traditional method of separation to get an oxygenated substance (citral). A simulation model of the distillation helps identify the optimal operating conditions. The objective of this simulation is to separate the oxygenated compounds from terpenes.

2.3.2.2 Menthol Recovery by Crystallization of Mentha Oil

Mentha oil contains menthol, a commercially important product. Menthol is separated from the other components on the basis of differences in melting temperatures. Crystallization from solution is an industrially important unit operation due to its ability to provide high purity separations.

The crystal growth and nucleation kinetic parameters must be determined experimentally before systematically designing a crystallizer and computing optimal operations and control procedures.

2.3.2.3 Carvone Recovery from Spearmint Oil

Spearmint oil contains the major component carvone that must be separated from other components. The separation of carvone is done by continuous distillation and the process is optimized after identification of the relevant parameters worked out by sensitivity analysis. The objective of this simulation is to obtain carvone at 95% purity or more.

2.3.2.4 Peppermint Oil Extraction by Steam Distillation

For the steam distillation of peppermint, the peppermint leaves are placed at the bottom of a distillation flask and steam is percolated through. The peppermint oil evaporates, and the emerging mixture of vaporized water and oil moves through a coil, usually cooled with running water, where the steam condenses. The mixture of condensed water and essential oil is collected and separated by decantation or, in rare cases, by centrifugation.

2.3.2.5 Multiple-effect Evaporation of Milk Serum

Evaporation is a widely used operation for the recovery of valuable products from dilute aqueous mixtures, such as milk serum. In this case, a four-effect process helps minimize the energy consumption and makes this process economically attractive. Key features are the effects of both pressure and heat transfer coefficients on the overall performance of the apparatus.

2.3.3 Case Study: Turpentine Oil Batch Distillation

Turpentine oil obtained from species of *Pinus* (family Pinaceae) is mainly used in paint and soap manufacturing industries, and in the pharmaceutical industry its use is limited to balms and oil bases. Semi-fluid mixtures of resins remain dissolved in the volatile oil, thus it is produced by fractional distillation. The objectives of the process simulation are to: (i) develop the process simulation base case, (ii) understand how to obtain complete fractionation of the oil, (iii) optimize the composition of pinene, carene and longifolene in the product streams, and (iii) optimize the time and energy consumption of the process.

Figure 3a shows the fractional composition profiles of pinene, carene and longifolene versus time obtained in the top of the distillation column. Figure 3b shows the instantaneous energy consumption of a constant reflux operation.

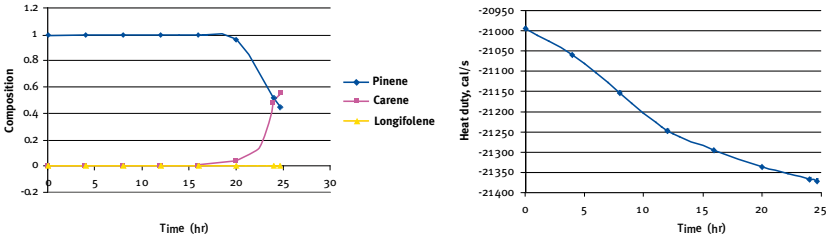


Figure 3: a) Fractional composition versus time, and b) Energy consumption versus time for the base case

Figure 4 shows the same process in which the reflux ratio is varied in order to obtain a constant composition at the top of the column. It is interesting to note that the distillation time as well as energy consumption are greatly reduced.

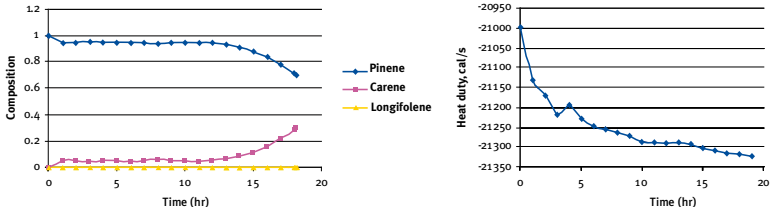


Figure 4: a) Fractional composition versus time, and b) Energy consumption versus time for the constant composition case

Figure 5 shows that a total separation of the oil constituents is achievable.

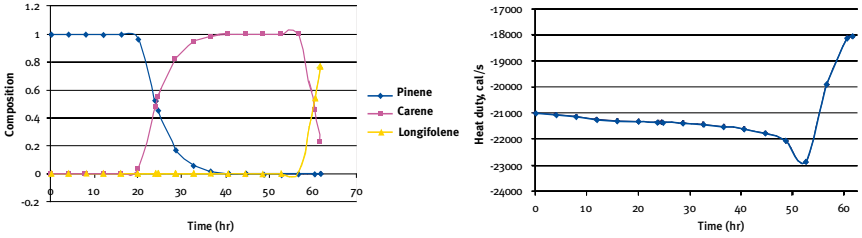


Figure 5: a) Fractional composition versus time, and b) Energy consumption versus time for the total fractionation case

These simulations show that, in the base case with a reflux ratio of 15 and a high consumption of energy (Figure 4), the distillate accumulator collects a high percentage of pinene (93%). If a PID controller is introduced to maintain the concentration constant, the composition of pinene is around 90% and it takes only 12 hours and a reflux ratio of 5 to achieve the desired value, thus saving time and energy. In the case of complete fractionation, we can collect 93% of pinene, 88% of carene and 5.7% of dump products at the end of the process.

2.3.4 Case Study: Menthol Recovery by Crystallization of Mentha Oil

Crystallization from solution is an industrially important operation due to its ability to provide high-purity separations. The menthol crystallization process using menthe oil is rather simple, and consists of a cascade crystallization as shown in Figure 6.

The objective of the simulation is to optimize the menthol crystallization process. The oil, composed of 75% menthol and also containing menthyl acetate, limonene and menthone (Table 1), is fed into the first crystallizer where the temperature is 35° F. The menthol crystals produced here are separated by decantation. The decanted liquid is passed to the second crystallizer and the crystals obtained in this second stage are also separated from the liquid by decantation. Thus, the assumptions made are: (i) limonene is present in all the fractions, and (ii) the separation of solid material from the liquid portion is complete. Furthermore, the thermophysical properties of menthone and menthyl acetate are included in the software's database. The feed stream conditions are: temperature, 80° F; pressure, 1 atm; and flow rate, 50 lb · mol/h.

Table 1: Major constituents of mentha oil

Constituent	Concentration
Menthol	75%
Menthyl acetate	11%
Limonene	8%
Menthone	6%

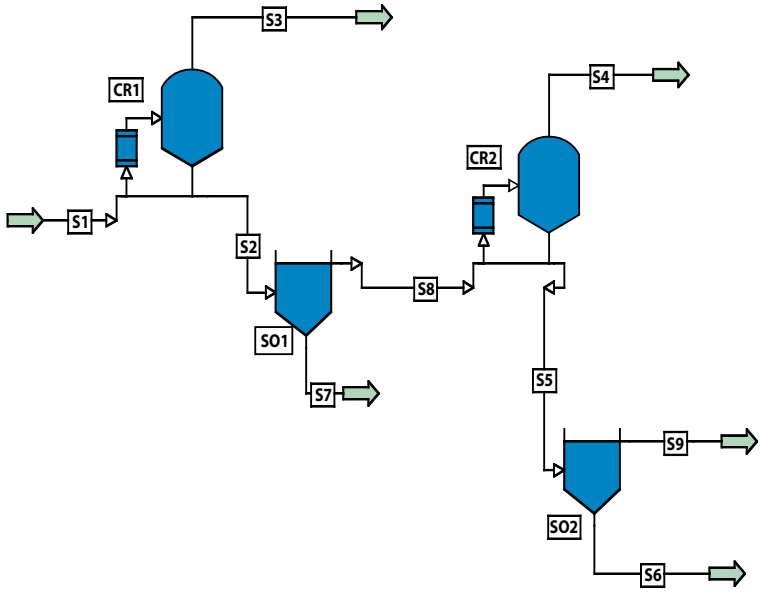
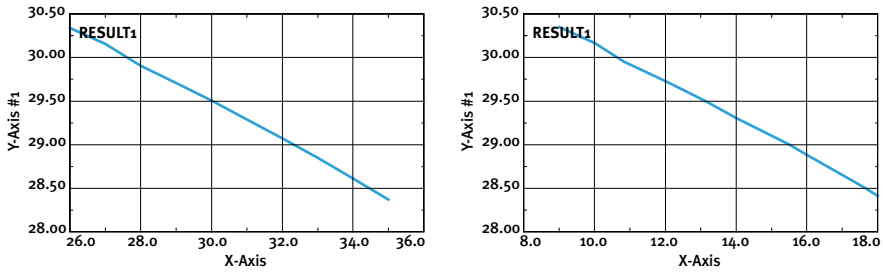


Figure 6: Flowsheet for the menthol crystallization process



a *b*

Figure 7: Variation of menthol flow rate (Y axis, lb mol/hr) as product of both crystallizers (S6 + S7) versus T (X axis, °F). a) Crystallizer 1. b) Crystallizer 2

Figures 7a and b show on the Y axes the total flow rate (lb mol/hr) of menthol crystal produced in both crystallizers (the combination of S6+S7 of Figure 6). It is evident from the sensitivity analysis that the temperature of the crystallizers has an effect on the total amount of pure product obtained, and consequently on the product yield. In fact, the base case (Table 2) reports a figure of 28.469 lb mol/hr and this amount can be raised linearly if the temperature of the crystallizers is lowered. The sensitivity analysis helps the engineer to select the right temperatures of the crystallizers for a given production.

The material and energy balance of the menthol extraction plant for the base case is listed in Table 2. This is an example of the simulator's output and these values may change if the process conditions are changed. In the first crystallizer, the menthol produced is equal to 5.633 lb mol/hr (purity one) and in the second crystallizer the amount is 22.836 lb mol/hr (purity one). If we compare the total amount of menthol produced by the two crystallizers (22.836 + 5.633 = 28.469 lb mol/hr) with the total amount of menthol fed to the process (37.5 lb mol/hr), we obtain a recovery (amount of pure menthol produced/total amount of menthol fed to the process) of 75.91%, which is rather satisfactory. Table 2 also reports the temperature, pressure, total flow and composition of each single stream considered in the process.

Table 2: Material and energy balance for the menthol crystallization process. The stream names refer to Figure 6

Stream name		**S1**	**S2**	**S5**	**S6**	**S7**	**S8**	**S9**
Phase		**Liquid**	**S/L**	**S/L**	**Solid**	**Solid**	**Liquid**	**Liquid**
Temperature	F	80	35	18	18	35	35	18
Pressure	PSIA	14.696	14.696	14.696	14.696	14.696	14.696	14.696
Molecular weight		159.170	159.170	161.608	156.270	156.270	161.608	163.004
Total	lb mol/hr	50.000	50.000	27.164	5.633	22.836	27.164	21.531
Component mole fractions								
D-limene		0.0800	0.0800	0.1472			0.1473	0.1858
Menthol		0.7500	0.7500	0.5399	1.000	1.0000	0. 5398	0.4195
Menthyl acetate		0.1100	0.1100	0.2025			0.2025	0.2554
Menthone		0.0600	0.0600	0.1104			0.1104	0.1393

2.4 Conclusions

There are two important benefits of the application of process simulation to phytochemical processes of industrial interest.

The first is to improve process knowledge. This is achieved by verifying "in silico" the operating conditions and the estimates of data for intermediate streams, which are difficult to measure. Process knowledge also includes: (i) enthalpy balance information, (ii) verification of plant specifications, (iii) influence of operative parameters on process specifications, (iv) validation of phase equilibrium models for the real system to be used in similar conditions, and finally (v) process de-bottlenecking for each section.

The second important benefit is process optimization, in terms of: (i) consumption of energy and raw materials, (ii) identification of process control strategies, and (iii) clarification of security system behavior when process conditions are varied.

Running process simulation software requires: (i) availability of thermodynamic properties for all components involved, (ii) definition of an accurate thermodynamic model (equations of state or excess Gibbs energy model) for binary and multi-component mixtures, (iii) availability of all necessary interaction parameters, (iv) availability of all necessary unit operation modules, and (v) identification of tear streams to achieve rapid convergence in case of recycles. Furthermore, sometimes it is necessary to define and develop user models and user thermodynamic models.

It is necessary to stress some important principles. First, the program is an aid in making calculations and decisions: the process engineer must ensure that it is "fit for purpose" and is responsible for the results generated and for any use which is made of the results. Second, it is the professional, ethical and legal responsibility of the process engineer to take care and to exercise good judgment. Process simulation is, in essence, a program.

Nonetheless, process simulation is important since it: (i) has high accuracy, (ii) allows one to focus on the interpretation of the results rather than on the methods for obtaining the results, (iii) allows a global vision of the process by assembling theories and models, (iv) is essential in the design of new and existing processes, (v) is essential in the analysis of existing plants in terms of environmental impact, and (vi) is a simple tool for treating real cases.

Process simulation is a well established tool in the chemical industry and has been used for a decade in the petrochemical industry. Process simulation is now applicable in many different fields besides the

petrochemical and fine chemical industries, and is particularly interesting for biotechnological and phytochemical processes.

In summary, process simulation may play an important role in the optimization of phytochemical processes and, therefore, application of process simulation can assist in the development of advanced processes. This paper showed that it is possible to achieve energy reduction and maximization of product yield.

Process simulation perhaps is not a good tool for countries that are using primitive techniques, since they should aim at reaching a stable quality of the product rather than an optimization of energy consumption and environmental issues. Moreover, they should focus on practical problems such as the quality of the materials and the water to be used for extraction.

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