Lignin Valorization Process Control under Feedstock Uncertainty through a Dynamic Stochastic Programming Approach

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Lignin Valorization Process Control under Feedstock Uncertainty through a Dynamic Stochastic Programming Approach

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The randomness introduced by reactants is an issue when processing renewable bioresources. In this paper we apply tools from dynamic stochastic programming theory to the biochemical process. Instead of introducing extra preprocessing units, we consider the inherent randomness of the process and optimize in expectation the performance of the system. In a general setting this is a multistage stochastic optimization problem and we investigate its approximate solution via two approaches, namely Stochastic Dual Dynamic Programming (SDDP) and the finite state, finite action Markov Decision Process (MDP) framework. These two methods are implemented to a case study of lignin valorization that is crucial to a cost-effective biorefinery process using biomass as the feedstocks.

Green technologies play a vital role on a sustainable society by providing renewable energy and renewable resources to reduce the dependence on fossilized carbon, and enabling benign processes to replace the polluting ones[1]. However, in spite of rapid technological advances to satisfy sustainability requirements[2,3], renewable energy and chemicals have only occupied a small fraction of energy and chemical market due to several drawbacks including generational discontinuity, complex and heterogeneous molecular structures, and high amount of impurities[4,5]. These unavoidable disadvantages are caused by the generating conditions for renewable resources such as weather, production conditions (e.g. soil, fertilizer, irrigation), storage conditions, as well as pretreatment and extraction processes.

Biomass is defined as all the organic matters that are derived from plants. Biomass energy currently contributes approximately $10-14\%$ of the world's primary energy supply and has the potential to contribute $30-40\%$ in 2050[6]. The non-edible biomass such as lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin. In comparison with other renewable resources (e.g. solar and wind), biomass has a unique distinguishing characteristic. Specifically, biomass can be converted to, in addition to relatively low-value energy, a variety of value-added platform chemicals and materials that help to mitigate environmental problems resulting from synthetic materials, and satisfy customers' special needs for product functionalities[7][8].

Lignin occupies $15\%-40\%$ of lignocellulosic biomass and is usually reclaimed as the low-cost waste from biomass-derived

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biorefinery processes[9]. The US paper industry alone produces more than 50 million tons of lignin per year with only 2% currently used for commercial products. The consensus is that the conversion of abundant waste lignin stream to high value byproducts is a feasible and necessary means for an economic-effective biorefinery process. As shown in Fig 1, lignocellulosic biorefinery process mainly focuses on the conversion of carbon sources such as biomass, starch, and algae to liquid fuels, platform chemicals, and materials via thermal/chemical or biological methods. In current biorefinery operations, lignin is either burned to produce low-cost heat for power generation or sold as the animal feeds in wet and dry corn mill. To better utilize lignin as the main waste stream of biorefinery process, more recent research has been focused on converting lignin to value-added byproducts. In particular, lignin, as the largest source of aromatic building blocks in nature, has significant potential to serve as the starting material for the production of platform chemicals that can replace petroleum-derived BTX (benzene, toluene, and xylene) for the production of functional bioproducts[10,11]. If biomass-derived biochemical techniques are commercialized as sustainable processes on a large scale[12], the biorefinery process will be able to produce 0.225 billion tones of lignin to replace up to 30% of the transportation fuel and chemical supply[13].

Lignin constitutes of monomeric phenyl propylene units to link together to form a crosslinking structure. During the recent decade, much effort has been devoted to valorization (or depolymerization) of lignin to high value aromatic monomers via oxidation, reduction, thermal-chemical and biological methods[14–18]. While it is well-known that the complexity of lignin structure and property has an important impact on its depolymerization chemistry, reaction parameters, and the yield and selectivity of final products, the quantitative relationship among the key lignin characteristics, reaction kinetics, and products output (yield and selectivity) has not been well-understood. Recently Ma et. al.[19] applied a multi-variable linear estimation method to establish the correlation between lignin structural properties and their conversion reactivity toward the oxidative depolymerization process. However, many factors have a non-linear relationship that is beyond this linear model analysis. Moreover, the chemical and molecular properties of lignin obtained from biorefinery processes vary significantly in different biomass species and different biorefinery and extraction processes[20–22]. How to minimize the negative effects of lignin's characteristic uncertainty on its valorization process has become a new challenge to guarantee stable yield and high quality of the depolymerized products.

From the mathematic point of view, numerous optimization methods have been applied to the field of sustainable energy and renewable resources. A variety of optimization techniques, including mixed-integer linear-programming, Lagrangian relaxation, quadratic programming, Nelder-Mead Simplex search, genetic algorithms, particle swarm optimization and pareto-based multi-objective-optimization, have been used to solve a few different design, planning, and control problems arising from this area[23,24]. Most of these studies focus on wind and solar energy system with homogenous resources rather than biomass with heterogenous structures and variable properties. Furthermore, a few studies on optimization methods for bioenergy have been directed to the energy management policy[25], the supply chain of biomass resources[26], and the distribution of the produced fuels and energy[27]. To the best of our knowledge, optimization methods to deal with uncertainty existing in biochemical processes have seldom been reported. In fact, the randomness in reactants has seldom been discussed even for conventional chemical processes, because these processes rarely handle impure reactants. Stochastic optimization approach has been studied to resolve certain randomness issues in process control when no reaction is involved[28]. By contrast, biochemical process has to deal with large randomness and impurity in reactants (e.g. lignin). In the presence of reactants the associated nonlinearity leads to continuous valued optimization problems that are difficult to solve. Thus, it is necessary to develop new and appropriate stochastic optimization methods to deal with this issue so that we can control the feedstock randomness, the major hinderance for the scale up of biochemical process.

This study formulates a stochastic process model to optimize process robustness through addressing uncertainty on reactants in a typical lignin valorization process. As illustrated in Fig. 2, lignin rich residues following the upstream biorefinery processes are randomly mixed from different sources, creating a stochastic lignin content profile in the mixing tank. Pump 1 then controls the inlet flow rate from the mixing tank to a reactor with fixed volume. The reactor operates at constant temperature controlled by the heating unit, with other reacting reagents (e.g., catalyst) added from the top. Powered by Pump 2, effluent from the reactor then feeds to an air cooler and further into the extraction column, where the final aromatic monomer products are generated by using organic solvent extraction.

Our previous research shows that biomimetic catalysts are attractive for the depolymerization of lignin to aromatic chemicals due to their low cost and relatively mild reaction conditions[29–31]. In particular, among these catalysts, the use of sodium persulfate-based biomimetic catalyst results in good yield and requires rel-
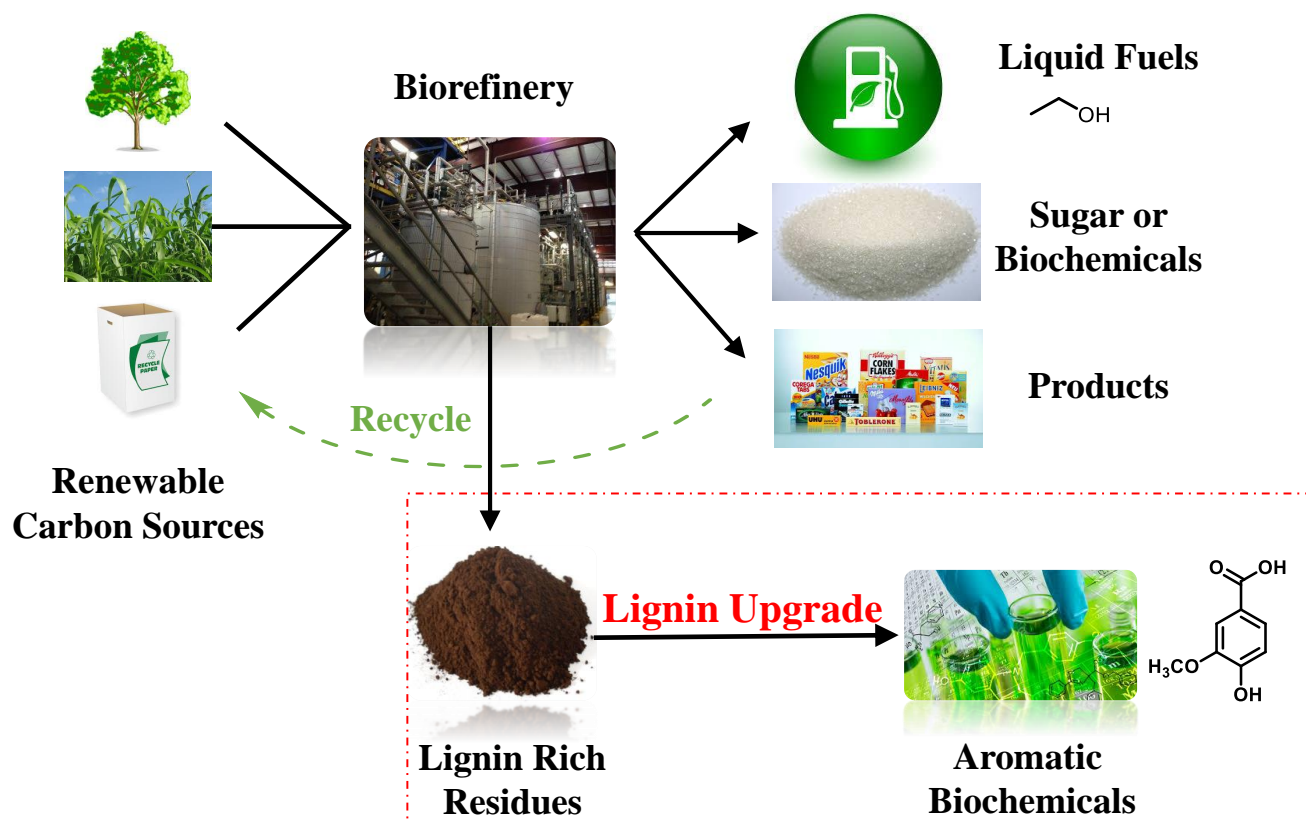
Fig. 1 The general biorefinery process for lignin extraction and upgrading.

ative milder conditions. Fig. 3 describes a plausible mechanism of this lignin valorization process using persulfate as the catalyst, which demonstrates that the cleavage of β-O-4 bonds by sulfate free radicals dominates this reaction. In this research, we further investigate the reaction kinetics of this process for both lignin model compounds and authentic lignin, which will be used to derive the dynamic equations later in our stochastic optimization model.

We elucidate the reaction kinetics, especially the relationship between the conversion yield and different levels of reaction parameters, through a set of experiments. The Box-Behnken method and response surface method, respectively, were used to design the experiments and analyze the obtained results in order to determine the effect of various reaction parameters on the conversion yield of lignin and the optimal reaction parameters (see the experimental section for more details). Our system operates under relatively mild condition ($60-100°C$, 1 atm) to con-

duct the lignin depolymerization process. Our results indicate that persulfate-based catalyst could effectively convert up to 99% lignin into aromatic monomers, and that a set of optimal reaction conditions achieving the smallest cost for the lignin valorization process are given by 2 h reaction time, $80°C$ reaction temperature, 2.0 mol equivalent persulfate loading and 5% Ferrous catalyst loading (based on persulfate)[31]. Moreover, maintaining other reaction conditions at the optimal level and varying the reaction time from 15 min, 30 min, 45 min, 60 min, to 120 min, we observed that the conversion yield of lignin increased from $37\%\pm5.4\%$, $69\%\pm3.0\%$, $87\%\pm2.6\%$, $93\%\pm2.0\%$, to $99\%\pm0.5\%$, respectively. These experimental results suggest that the lignin valorization reaction follows the first order kinetic model defined as

$$r = -\frac{dc}{dt} = k_r c, \qquad (1)$$

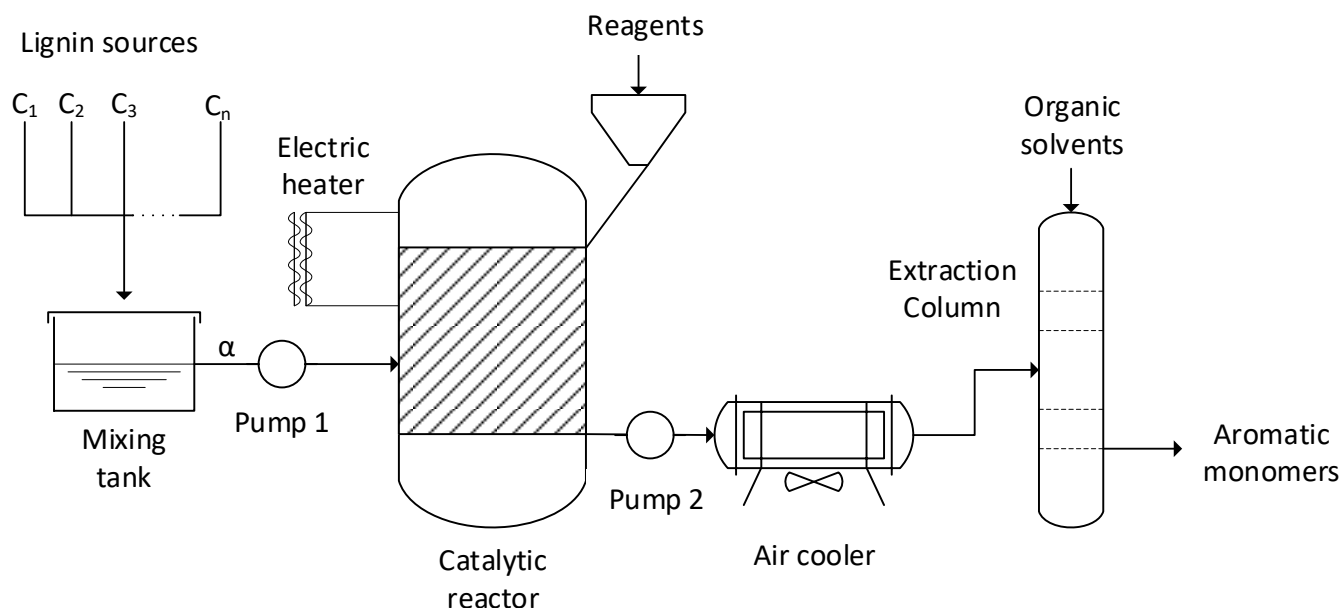where c denotes the reactant concentration, r denotes the re-

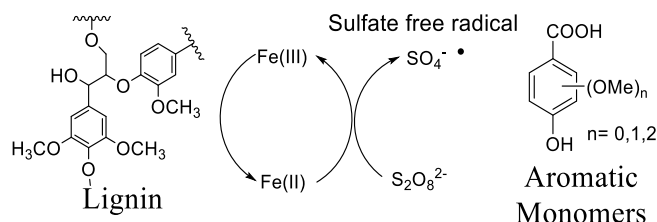**Fig. 2** Lignin oxidative depolymerization process design.

Fig. 3 Lignin oxidative depolymerization by biomimetic oxidative catalyst.

Table 1 Reactor design for stage i

1	Initial reactant concentration c_{i-1}
2	React at volume V for the time of a stage ΔT
3	Feed the reactor with inlet flow rate f_i in time t, collect effluent stream with the same flow rate to maintain the constant volume V
4	Forward to stage $i+1$

action rate, and k_r denotes the rate constant for this reaction. We can directly calculate the reaction rate constant k_r according to (1) and the experimental data. The dependence of k_r on other reaction conditions, e.g., temperature, can also be derived using the Arrhenius equation

$$k_r = A\,exp(-E_a/RT),$$

where A denotes pre-exponential factor, E_a denotes activation energy for the reaction, R is the universal gas constant and T is the absolute temperature. Specifically, the activation energy E_z of β-O-4 compound can be computed according to Jiang et. al.[32].

As shown in Table 1, the reactor design follows a stage wise operation which conforms the kinetics in (1). At stage i the initial reactant concentration is c_{i-1} and reacts at volume V for the dura-

tion ΔT. Within this stage the reactor is fed with inlet flow rate f_i for a duration t and the effluent stream is collected with the same flow rate to maintain the constant volume V. Then the next stage $i+1$ ensues. It should be noted that if $t = \Delta T$, then feeding, reaction and draining will happen simultaneously. Otherwise, feeding and draining will occur in the beginning of the reaction at stage i although the reaction will continue for the whole stage. Our model covers both situations mentioned above. The reaction consumes reactant over time which brings the concentration of reactant down to a lower level. Let us consider the reaction at stage i lasting for time ΔT. By rearranging the terms in the equation (1) and taking the integral on both sides, we obtain

$$-\int_{c_{i-1}}^{c_i'} \frac{1}{c}dc = \int_0^{\Delta T} k_r dt.$$

Solving the above equation via integration yields

$$c_i' = c_{i-1} exp(-k_r \Delta T), \qquad (2)$$

where c_{i-1} and c_i' denote the initial concentration and the concentration after reaction at stage i, respectively. Now consider the operation at the end of stage i. We calculate the mass balance of lignin contents according to

$$Input + Generation = Output + Accumulation + Consumption.$$

The reaction is irreversible at fixed volume and the generation of lignin equals to 0. For the reaction in this stage, the consumption of lignin can be written as $(c_{i-1} - c_i')V$. Since the reactor is fed with inlet flow rate f_i for a duration t while effluent stream is kept at the same flow rate, it is easy to see that $\alpha f_i t$ represents input and $c_i' f_i t$ represents output where α denotes the abundance of reactant in the feed. Feeding operation is to replenish lignin for the next stage reaction, thus the difference $(c_i - c_{i-1})V$ represents accumulation where V denotes the volume of the reactor. We can write the mass balance equation for stage i as

$$\alpha f_i t = c_i' f_i t + (c_i - c_{i-1})V + (c_{i-1} - c_i')V. \qquad (3)$$

Rearranging the above equation and substituting c_i' with equation (2), we obtain an equation on the final concentration of reactant at the end of stage:

$$c_i = c_{i-1} exp(-k_r \Delta T) \left(1 - f_i \frac{t}{V}\right) + \alpha f_i \frac{t}{V}, \ i = 1, \ldots, N_T. \qquad (4)$$

We observe that the reactant abundance α in (4) is random, because lignin contents distribute unevenly in different biomass species as the feedstocks of the valorization process. To model the randomness of α, we considered twenty different species, including Wheat Straw, Rice Straw, Rye Straw, Hemp, Tall Fescue Stems, Tall Fescue Internodes, Flax, Jute, Sisal, Curaua Leaf Fiber, Banana Plant Leaf, Piassava Fiber, Abaca, Loblolly Pine, Spruce, Eucalyptus globus, Eucalyptus Grandis, Birch Pendula, Beech and Acacia. The percentage of guaiacyl (G), p-hydroxyl phenol (H) and syringyl (S) lignin in all sources of biomass was obtained from Ragauskas et. al.[33]. The β-O-4 bonds are the most abundant bonds in all types of lignin with smaller amounts of β-5, β-β, and other minor linkages. According to previous study, the β-O-4 bond percentage in softwood species was 50% and in hardwood ones was 65%[34]. Eventually a series of concentration profiles were generated to indicate the abundance of the active chemical bond (β-O-4) in each lignin feedstock, whose cleavage dominates the lignin valorization reaction in view of our reaction mecha-

nism. In addition, the entire process was assumed to operate at a weight loading of 10 g lignin per liter of solvent. A random mix of different kinds of lignin was assumed to simulate randomness in real operation. Several statistical distribution models were fitted into the set of concentration profiles to give descriptions of the variety of authetic lignin, including Weibull, Birnbaum Saunders, Exponential, Gamma, Rayleigh, Inverse Gaussian, Log logistic, Nakagami and Rician distribution. In terms of Maximum Likelihood Estimation the Weibull distribution with parameters $\alpha_\mu = 11.162$ and $\alpha_\sigma = 1.82309$ gave the best fit. This continuous distribution served as a random sample generator when simulating the lignin valorization process.
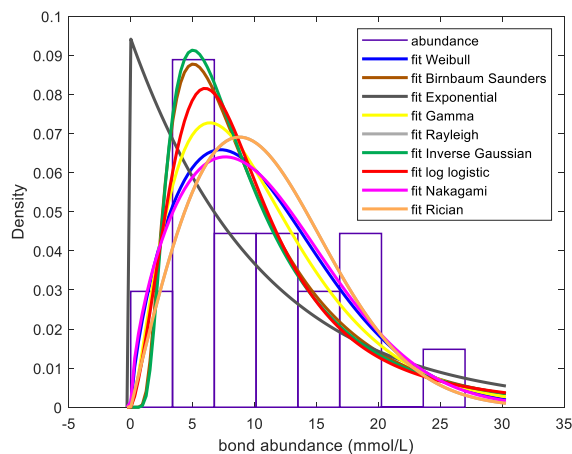

Fig. 4 Diagram for lignin β-O-4 content distribution.

Our control variables are the inlet flow rates f_i at stages $i = 1, \ldots, N_T$ measured in (L/s), and the initial abundance of linkage in the reactor, c_0 (mol/L). Stochasticity is induced by the variable α abundance of linkage in the feed (mol/L). We would like to use these control variables to minimize the total expected deviation from predetermined target levels denoted by $\hat{c}_0, \ldots, \hat{c}_{N_T}$. This is a discrete time stochastic optimization problem with continuous valued state variable $c_i \in \mathscr{C} = [c_{min}, c_{max}], i \in \{1, \ldots, N_T\}$ and continuous valued control variables $f_i \in \mathscr{F} = [f_{min}, f_{max}]$, $i \in \{1, \ldots, N_T\}$ and $c_0 \in \mathscr{C}$. The minimization problem is

$$\min_{c_0 \in \mathscr{C}, f_1 \in \mathscr{F}, \ldots, \ldots, f_{N_T} \in \mathscr{F}} \mathbb{E}\left[|c_0 - \hat{c}_0| + |c_1 - \hat{c}_1| + \ldots |c_{N_T} - \hat{c}_{N_T}|\right] \qquad (5)$$

subject to the constraints imposed by the nonlinear stochastic dynamics (4) and $c_i \in \mathscr{C}, i \in \{1, \ldots, N_T\}$. The expectation is calculated with respect to the joint distribution of the independent identically distributed random variables $\alpha_1, \ldots, \alpha_T$. The difficulty

of this problem is induced by the nonlinear stochastic dynamics, the presence of constraints on the state and control variables and the fact that the policies are functions with continuously valued domains and ranges.

Two stochastic optimization methods are implemented to find the approximate optimal solution of the problem. The first method is a Markov decision process (MDP) formulation with finite state and control spaces obtained via discretization and the second one is the stochastic dual dynamic programming (SDDP) algorithm[35]. These optimization methods create a dynamic predictive model that helps us to control the process parameters (e.g. flow rate, time, reactant concentration) to achieve a good and uniform yield of the final bioproducts. Each of these methods has its own merits which are discussed later when we compare by means of simulations. These methods can be further extended to multiple input and output case and other sustainable processes beyond lignin depolymerization process.

First we discuss the (MDP) model, obtained via discretization. In the MDP formulation c_0 is treated as a parameter while the control values $f_1, \ldots, f_{N_T}$ are determined via policies $\mu_i : \mathscr{C} \to \mathscr{F}$ in the sense that

$$f_i = \mu_i(c_i), \ i = 1, \ldots, N_T.$$

The state space $\mathscr{C}$ is the concentration of the material in the tank, we discretize the concentration's range into N states, i.e., $S := [s_1, \ldots, s_N]$, where $s_1 = c_{min}$ and $s_N = c_{max}$. The values of the inflow rate $\mathscr{U}$ are also discretized into L actions, i.e., $U := [u_1, \ldots, u_L]$, where $u_1 = f_{min}$ and $u_L = f_{max}$. We also introduce the constant

$$b = exp(-\Delta T A exp(-E_a/RT))$$

to save on notation. The value function is given by

$$V_{N_T-1}[c_{N_T-1}] = \min_{f_{N_T} \in U} \mathbb{E}_{\alpha_{N_T}} [\ |c_{N_T} - \hat{c}_{N_T}|]$$

and for $t = 1, \ldots, N_T - 1$,

$$V_{t-1}[c_{t-1}] = \min_{f_t \in U} \mathbb{E}_{\alpha_t} [|c_t - \hat{c}_t| + V_t[c_t]]$$

s.t. $c_t = bc_{t-1}(1 - f_t t/V) + \alpha_t \frac{f_t t}{V}$. The value function itself is computed via the value iteration algorithm, which is a backward algorithm and delivers as a byproduct the optimal policy as well. At this point it is worth mentioning that the Markov chain modeling method in the uncontrolled case was widely used to analyze complex models in chemical engineering, environmental engineering[36] and biological engineering. Applications of discrete Markov chain models in chemical reactions, chemical reactors

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Algorithm 1 Value iteration

1. Start from stage N_T-1, compute the value function $V_{N_T-1}[c_{N_T-1}], \forall c_{N_T-1} \in S$.

for $c_{N_T-1} = s_1, \ldots, s_N$
    for $f_{N_T} = u_1, \ldots, u_L$
    Compute

$$\mathbb{E}_{\alpha_{N_T}} [|c_{N_T} - \hat{c}_{N_T}|], \text{ where } c_{N_T} = bc_{N_T-1}(1 - f_{N_T}t/V) + \alpha_{N_T} \frac{f_{N_T}t}{V}. \tag{6}$$

    end for
Choose the f_{N_T} that minimizes (6) as the optimal action at the corresponding state c_{N_T-1}, thus obtaining the optimal policy μ_{N_T} and the corresponding value (6) is $V_{N_T-1}[c_{N_T-1}]$.
end for
2. Go back to stage $N_T - 2$, we compute the value function $V_{N_T-2}[c_{N_T-2}], \forall c_{N_T-2} \in S$ and the corresponding optimal policy μ_{N_T-1}. Use the same procedure as in step 1, and keep going backwards until stage 0.

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and complex chemical processes are described in Tamir[37]. Our contribution is the use of the Markov chain modeling technique in conjunction with the presence of control inputs leading to the aforementioned MDP formulation and the associated algorithm for computing optimal control values as functions of the state. We now proceed to discuss the SDDP algorithm. First we need the following lemma about McCormick relaxation[38] to linearize the bilinear term $c_{N_t-1}f_{N_t}$ in the relation (4).

Lemma 1 *Consider the set $B = \{(w,x,y) \mid x^L \leq x \leq x^U, y^L \leq y \leq y^U, w = xy\}$ and the polyhedral set C described by the following inequalities*

$$w \geq x^U y + xy^L - x^L y^L$$

$$w \geq x^U y + xy^U - x^U y^U$$

$$w \leq x^U y + xy^L - x^U y^L$$

$$w \leq xy^U + x^L y - x^L y^U,$$

then $B \subset C$.

With the above relaxation the multi-stage stochastic optimization

problem can be decomposed by time stages as follows

$$\min_{x_0} F_0(x_0) + \mathbb{E}\left[\min_{x_1}F_1(x_1) + \ldots \qquad + \min_{x_{N_T}}F_{N_T}(x_{N_T})\right]$$

s.t. $x_0 \in X$　　　s.t. $A_1x_1 = b_1 + B_1x_0$　　　s.t. $A_{N_T}x_{N_T} = b_{N_T} + B_{N_T}x_{N_T-1}$

$$x_2 \in X \qquad\qquad x_{N_T} \in X,$$

(7)

where $x_i = (c_i, f_i, u_i, s_i^1, s_i^2, s_i^3, s_i^4), \forall i = 1, \ldots, N_T$, $F_i(x_i) = |c_i - \hat{c}_i|$,

$$A_i = \begin{pmatrix} 1 & (b-\alpha)t/V & -bt/V & 0 & 0 & 0 & 0 \\ 0 & c_{max} & -1 & 1 & 0 & 0 & 0 \\ 0 & c_{max} & -1 & 0 & 1 & 0 & 0 \\ 0 & c_{max} & -1 & 0 & 0 & -1 & 0 \\ 0 & c_{min} & -1 & 0 & 0 & 0 & -1 \end{pmatrix}$$

$$B_i = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -f_{min} & 0 & 0 & 0 & 0 & 0 & 0 \\ -f_{max} & 0 & 0 & 0 & 0 & 0 & 0 \\ -f_{min} & 0 & 0 & 0 & 0 & 0 & 0 \\ -f_{max} & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, b_i = \begin{pmatrix} 0 \\ c_{min}f_{min} \\ c_{max}f_{max} \\ c_{max}f_{min} \\ c_{min}f_{max} \end{pmatrix}.$$

This problem can be formulated equivalently in the form of dynamic programming:

$$Q_t(x_{t-1}, \xi_t) = \inf\{c_t^T x_t + \mathcal{Q}_{t+1}(x_t) : A_t x_t = b_t + B_t x_{t-1}\}, \qquad (8)$$

where $\mathcal{Q}_{t+1}(x_t) := \mathbb{E}\{Q_{t+1}(x_t, \xi_{t+1})\}$ and $\xi_t := (c_t, A_t, B_t, b_t)$ are random variables.

In the following we provide the SDDP algorithm to solve the above linearized stochastic programming problem.

Algorithm 2 SDDP Algorithm

---

1. **Initial:** starting point $(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_T)$, approximation of value function $\mathcal{Q}_t$ for $t = 1, \ldots, T$.

2. **Forward step**
   for t = 0 to T
   　for j = 1 to M
   　Compute $\bar{x}_{tj}$ as an optimal solution of the subproblem

   $$\min F_{tj}(x_t) + \mathcal{Q}_{t+1}(x_t)$$

   $$s.t.\ A_{tj}x_t = b_{tj} + B_{tj}\bar{x}_{t-1}.$$

   　end
   end
   and compute $\mathscr{V}_j := \sum_{t=1}^T F_{tj}(\bar{x}_{tj}), \forall j = 1, \ldots, M$.

3. Compute the confidence interval $\left[\bar{\mathscr{V}} - z_{\alpha/2}\hat{\sigma}_v/\sqrt{M}, \bar{\mathscr{V}} + z_{\alpha/2}\hat{\sigma}_v/\sqrt{M}\right]$, where

   $$\bar{\mathscr{V}} := \frac{1}{M}\sum_{j=1}^M \mathscr{V}_j \text{ and } \hat{\sigma}_v^2 := \frac{1}{M-1}\sum_{j=1}^M(\mathscr{V}_j - \bar{\mathscr{V}})^2.$$

4. Compute $\underline{\mathscr{V}} := \inf_x\{F_0(x) + \mathcal{Q}_2(x)\}$. Terminate if $\underline{\mathscr{V}} > \bar{\mathscr{V}} - z_{\alpha/2}\hat{\sigma}_v/\sqrt{M}$.

5. **Backward step**
   for t = T to 1
   　for j = 1 to N_t
   　Compute $\hat{x}_{tj}$ as an optimal solution of the subproblem

   $$\min F_{tj}(x_t) + \mathcal{Q}_{t+1}(x_t)$$

   $$s.t.\ A_{tj}x_t = b_{tj} + B_{tj}\bar{x}_{t-1}$$

   　and $\hat{\pi}_{tj}$ as an optimal solution of its dual problem. Define the cut $l_t(x_{t-1}) := \tilde{Q}_t(\bar{x}_{t-1}) + \tilde{g}_t^T(x_{t-1} - \bar{x}_{t-1})$, where

   $$\tilde{Q}_t(\bar{x}_{t-1}) = \frac{1}{N_t}\sum_{j=1}^{N_t} F_{tj}(\hat{x}_{tj}) + \mathcal{Q}_{t+1}(\hat{x}_{tj}) \text{ and } \tilde{g}_t = \frac{1}{N_t}\sum_{j=1}^{N_t} B_{tj}^T\hat{\pi}_{tj}.$$

   　Update $\mathcal{Q}_t(\cdot) = \max\{\mathcal{Q}_t(\cdot), l_t(\cdot)\}$.
   　end
   end

6. Go to step 2.

Note that in the above algorithm we obtain an "open-loop" policy, i.e. a sequence of optimal parameters $c_0, f_1, \ldots, f_{N_T}$.

To test our models and algorithms, we assume that a continuous lignin depolymerization reacting process ran in an operation of 2 days. Length of each stage was set as 30 minutes. Therefore, the operation consists of 96 stages. Both SDDP and MDP

algorithm were tested using same reaction parameters. Three different operating scenarios were assumed to simulate different operating conditions. The test was compared to a control test result. The control set assumed no randomness was involved in the reactant, and therefore the mean value of inlet concentration was used to directly calculate the operation for each stage. The first operating scenario assumed the target reactant concentration was kept at a constant level over the entire operation. The scenario simulates an ideal operation to produce single grade of product,shown in Fig. 5. The second scenario assumed four reactant concentration levels were required at different time for each day, which required adjustment on the target every 12 stages as Fig. 6 shows. This scenario simulates an operation to produce multiple grades of product using the same reactor. The last scenario in Fig. 7 assumes the target level changes at every stage, and is used exclusively to test the ability of controlling for each algorithm.
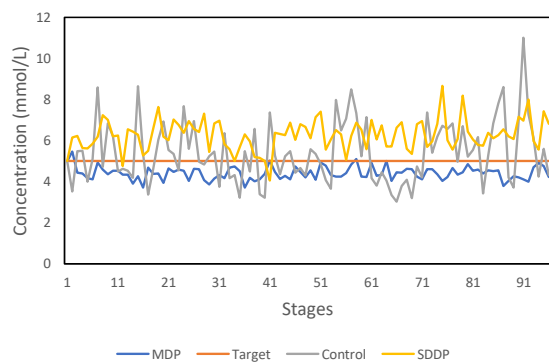

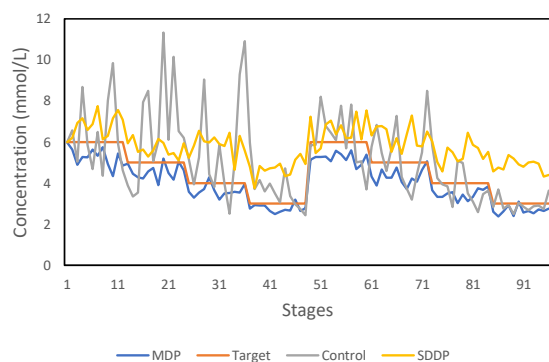**Fig. 5** Constant target concentration for all stages

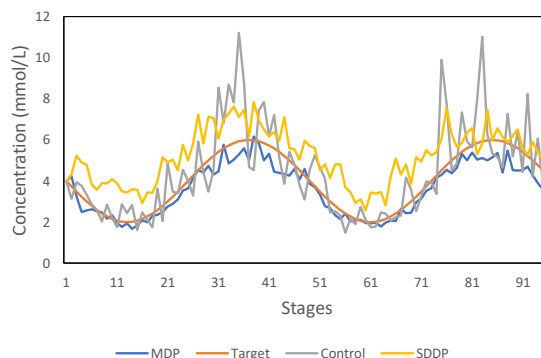**Fig. 6** Target concentration changes stage-wise

Fig. 7 Target concentration changes at each stage

Table 2 Performance summary

Operating Scenarios	Objective value			CPU times	
	MDP	SDDP	Control	MDP	SDDP
1	57.43	124.24	134.36	228.53	1646.1
2	51.33	125.17	116.19	228.97	1607.2
3	39.71	117.47	99.18	234.89	1619.1

Performances of both algorithms are listed in Table. 2. Compared to the control set, the results obtained from stochastic optimization show that both algorithms reduced total error over the entire operation. The SDDP algorithm takes relatively long time to calculate the optimal result, due to frequently calling solver to solve the convex subproblem for each stage. MDP algorithm discretized the operation, which simplified the process. Compare to the SDDP algorithm, the greatest advantage is the MDP approach can deal with nonconvex problem and only need to run one backward step, while the SDDP can only deal with convex problem and needs to iteratively run forward and backward steps. The numerical results also show the processing time of MDP is much smaller than the one of SDDP approach.

Conclusions

The results show that the MDP algorithm is appropriate for this specific sustainable chemical processing problem. This is proved by better objective value and relatively fast processing time of MDP. However, the SDDP algorithm assumes stage wise independence which enables a global approximation of the value functions using cutting plane models without requiring any direct discretization. This makes SDDP a viable choice when modeling complicated process. This could benefit when the model considers more parameters that have direct effects on

the reaction. In practice, the biobased feedstocks (e.g. lignin) usually include more uncertainty except an inter-unit β-aryl ether β-O-4 linkage[39] such as chemical compositions, structures and molecular weights. This work will serve as the pioneer work to use stochastic optimization methodology to optimize and control the randomness of feedstock in sustainable processes. In the future, we will focus on the seeking the appropriate dynamic stochastic programming method for the sustainable processes with more parameters of uncertainty.

Experimental

Oxidative degradation of β-O-4 lignin model compounds (1,3-Propanediol, 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-, (1R,2S)-rel-, CAS number 7572-98-7) with sodium persulfate was conducted under mild conditions. In a typical reaction, 10 mL water solution of 2.0 equivalent (EQ) mol of sodium persulfate were added into the glass vial at first, lignin model compound with ferrous aqueous solution (5% based on the molar ratio to persulfate) were then added into the reaction vial. The vial was sealed and placed in an oil bath maintained at $80°C$ under 500 rpm stirring. After the reaction is terminated, the product was extracted by ethyl acetate for Gas Chromatography–Mass Spectrometry (GC-MS) analysis. Two types of lignin including alkali lignin (Sigma-Aldrich) and organosolv lignin (extracted in our lab) were used as the feedstocks for the depolymerization reaction as well. In a typical run, 200 mg lignin sample was dissolved in a 10 mL ethanol (50 $wt.\%$) and then loaded into a seal tube. 2.0 equivalent (EQ) of persulfate (weight based) and 5% molar fraction of Ferrous catalyst was then added in the tube and the reaction temperature was increased to $80°C$ to initiate the reaction. The reaction was maintained for 24 hours. Samples were taken out from the seal tube after 3 h and 6 h reaction for gel permeation chromatography (GPC) analysis. The product after the reaction was extracted by ethyl acetate for three times and washed with water and brine. The organic liquid was evaporated in a rotary evaporator to remove the solvent and obtain the oil product.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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TOC

Herein we address the feedstock uncertainty for a robust lignin valorization process through a dynamic stochastic programming approach.

Controlling algorithm

$$\min|c_0 - \hat{c}_0| + \mathbb{E}[\min_{f_1}\{|c_1 - \hat{c}_1| + \cdots + \mathbb{E}[\min_{f_T}|c_T - \hat{c}_T|]\}].$$

Biochemical monomers

Biomass   **Reactor**