Diversifying Simulation Tools in CHEMCAD NXT: The Supercritical Solvent Extraction of Hemp Oil Case

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Industrial cultivation and harvest of plants within the cannabis genera were prohibited in the United States for decades; prohibition began in 1937, and was reinforced in 1970 under the Controlled Substance Act. Recent legislative advances, beginning with the Agricultural Act of 2014 and followed by the Agriculture Improvement Act of 2018, Pub. L. 115-334, have encouraged renewed interest in the plant *Cannabis sativa*. The interest ranges from consumer durable goods to valuable plant extracts.

As subspecies of *C. sativa,* the unique chemotaxonomic varieties determine the regulatory status of the plant which is to be harvested and processed. Compositionally, some varieties include higher levels of fiber while others see elevated levels of oils, cannabinoids, or other useful extracts. The specific cannabinoid delta-9 tetrahydrocannabinolic acid (THCA), or its post-carboxylated counterpart delta-9-tetrayhydrocanninol (THC), typically found in these genera serve as deterministic compounds for the legal legitimacy of the strain. It is also on this basis that processing methods and subsequent licensing instructions are governed for each of the states.

Many of the hemp products still require FDA approval for safe and effective use in treating any specific medical conditions. Cannabidiol (CBD) is one such cannabinoid of interest that has generally been found in high concentrations in the strains being cultivated today. Furthermore, there is interest in subsequent isolation of other unique cannabinoids such as cannabinol (CBN) and cannabigerol (CBG).

Various extraction technologies for plant oil separation are commercially viable and available to processors. In the case of hemp oil extraction, two solvent systems are overwhelmingly employed: ethanol and supercritical carbon dioxide (SC-CO_2). The ethanol route offers a simple process design, but due to its inherent flammability, requires that proper precautions be built into any system or facility. It is also non-selective for other undesirable plant compounds such as pigments or phenolics. SC-CO_2 and near critical CO_2 have the advantages of being non-toxic, leaving no residue upon depressurization, and lending themselves well to solubility adjustments by manipulation of temperature and pressure of the system.

The aim of this evaluation is to illustrate several capabilities in CHEMCAD NXT that permit users to methodically evaluate steps in typical hemp oil extraction and purification operations. Given the variation in strains and respective compositions, a preceding simulation would be beneficial in supporting a potential operation.

Preliminary Evaluation of CO₂ Parameters

Every compound has an intrinsic critical temperature and pressure for which phase boundaries exist. When the substance enters a region above both such critical points, separation of phases is no longer visible, and the fluid is considered supercritical. Values for fluid density are in the order of magnitude of liquids at atmospheric pressure, but the substance also exhibits diffusivities and viscosities similar to gases. The resulting densities, coupled with affinity for non-polar, low molecular weight compounds, permit the SC-CO₂ to be used to extract several valuable products from fibrous, high molecular weight plant material. A phase diagram with noted critical points is depicted in Figure 1.
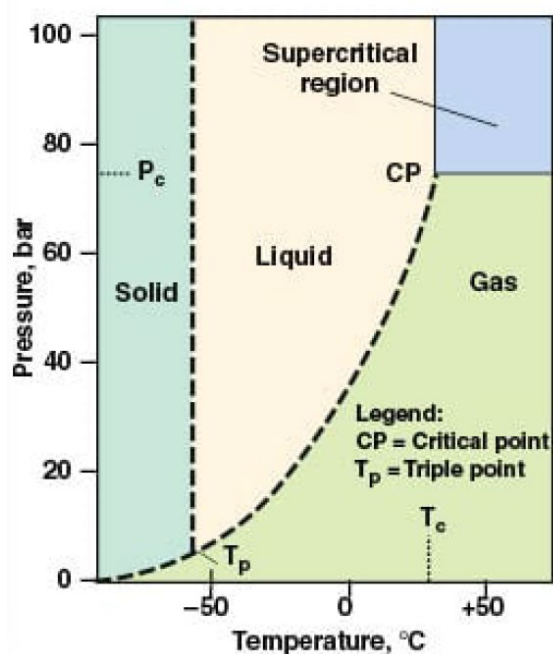

Figure 1: Phase Diagram for Carbon Dioxide [5]

The first analysis to be conducted would be miscibility regions of any constituent to be established within the SC-CO₂ matrix. This can be accomplished by visual inspection of binary P-x-y diagrams generated at potential operating temperatures. The evaluation of components can range from any entrainers to terpene products.

To start with a basic example, ethanol can be used as an entrainer to enhance oil removal from the hemp material in the SC-CO₂ system. The ethanol and carbon dioxide components are first added to the project simulation. For a binary system to be evaluated in supercritical conditions, Peng-Robinson is a suitable equation of state (EOS) choice while operating in the supercritical region shown in Figure 1. Next, a simple flowsheet is created with an inlet and outlet stream and a unit operation such as a pipe.

The process flow diagram in Figure 2 shows a pipe inserted with very low pressure drop conditions. For more information on the specific form of the Peng-Robinson EOS in CC-NXT (and prevailing mixing rules), consult the Help file article on the same topic.
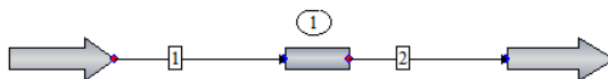

Figure 2: Simple process flow diagram showing a pipe UnitOp with one inlet and one outlet stream

On the CC-NXT Home ribbon, the path followed is **Charts** > **TPXY**. The *P-x-y* diagram at 120 °F is selected with carbon dioxide and ethanol as the first and second component, respectively. The mole fraction range should be set between 0.05 to 0.9. The plots and associated data will be available for viewing. In this case, no convergence issues are reported. This exercise should be repeated at 150 °F. The resulting bubble charts are shown below.
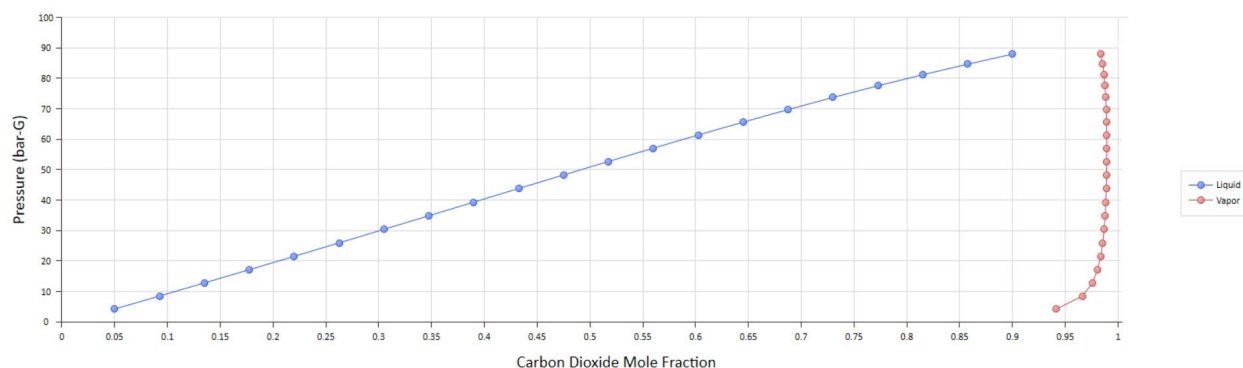
Figure 3: Carbon dioxide/ethanol bubble phase diagram evaluated at 120 °F using Peng-Robinson

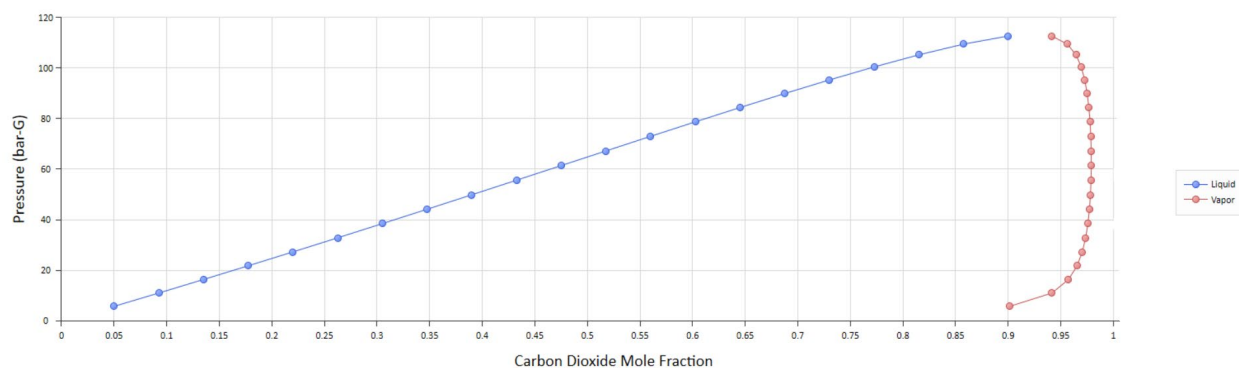*Figure 4: Carbon dioxide/ethanol bubble phase diagram evaluated at 150 °F using Peng-Robinson*

Visually, a critical locus can be projected between the vapor and liquid phase data series. However, in the case of the 120 °F isotherm in Figure 3, this point is not necessarily obvious. On a practical level, the locus in the 150 °F chart is more apparent (about 118 bar), and would suggest that this temperature is

more suitable for full miscibility of the SC-CO_2 with ethanol entrainer when designing the solvent system. Under this pressure, the system is subcritical and the potential for phase separation exists. Note the impact of a second component on supercritical pressure when compared to the pure SC-CO_2. This

miscibility technique can be applied for a variety of low molecular weight compounds combined with SC-CO_2. Full entrainer, or co-solvent selection within SC-CO_2 systems, is reserved for other reviews.

Phase behavior becomes more difficult to predict as the components are either more complex or unavailable in the compound database. Most often, only partial miscibility, or solubility, of any desired compound in the SC-CO_2 system is observed during an extraction. Although EOS approaches to evaluating solubility are plausible, alternative density-based correlations are often employed. This approach permits users to empirically determine solubility of both pure components or mixtures thereof and simply regress the resulting data according to the supercritical solvent properties.

One foundational approach was the experimental work of Chrastil for correlating solubilities of both liquids and solids in supercritical fluid solvents [1]. He theoretically assumed that molecules in a solute A associate with k number of molecules of the gas B in equilibrium according to a solvato complex AB_k, taking the form as follows:

$A + kB \rightleftharpoons AB_k$ Eq. 1

$K = \frac{[AB_k]}{[A][B]^k}$ Eq. 2

where [A] is the molar vapor concentration of the solute, [B] is the molar concentration of a gas, and $[AB_k]$ is the molar concentration of solute in a gas. K is the equilibrium constant. Further development of the equation leads to the final form:

$c = d^k e^{\frac{a}{T}+b}$ Eq. 3

where c is the concentration of a solute in gas in g/L, d is the density of the gas in g/L, k is an association number, a = ΔH/R, and b = ln (M_A+kM_B) + q − k ln M_B. The ΔH term is the enthalpy of solvation and vaporization; M_A and M_B are molecular weights of components A and B respectively. Generally, the terms a, q, and k are determined experimentally depending on the system. It should be noted that several researchers have modified Equation 3 to best suit the parameters of the system, but generally begin here.

In this vein, the SC-CO_2 density is now the key parameter to determine an operating condition for the extraction. When evaluating pure SC-CO_2 properties, as well as compression and transport thereof, the Benedict-Webb-Rubin-Starling (BWRS) equation of state is recommended. In CC-NXT, the 11-parameter BWRS equation suitably predicts physical properties of pure or high percentage CO_2 mixtures above critical conditions. Density is included in this. Using CC-NXT, a convenient method for generating several SC-CO_2 density ranges is possible using the Sensitivity tool under the Analysis tab.

Following the basic process flow diagram above, pure carbon dioxide should be specified in the feed stream. A new sensitivity analysis is created with two independent variables for adjusting stream 1. The first variable is pressure and the second, optional variable is temperature. The variable units are pressure and temperature, respectively. In this simulation, the units of pressure are bar while temperature was set to degrees F. The pressure is set to vary between 80 to 600 bar in 20 equal steps, and temperature is set to vary between 90 (slightly above critical) and 270 °F in 6 equal steps. Only one recording is necessary here for the resulting density of stream 2. Being mindful of a singular supercritical phase, CC-NXT reports the resulting densities in the vapor phase. The recorded variable should be vapor actual density (variable 31) with units of vapor density.

After the sensitivity analysis is created, ensure that its name is selected in the ribbon, then click **Run All**. When the run is complete, click **Plot Results**. For improved visibility of all isotherms, select the Surface chart type, with Pressure on the X axis and Density on the Y axis. Temperature should be the Z axis, and the 2-D projection box should be checked. The resulting series of isotherms is shown in Figure 5.
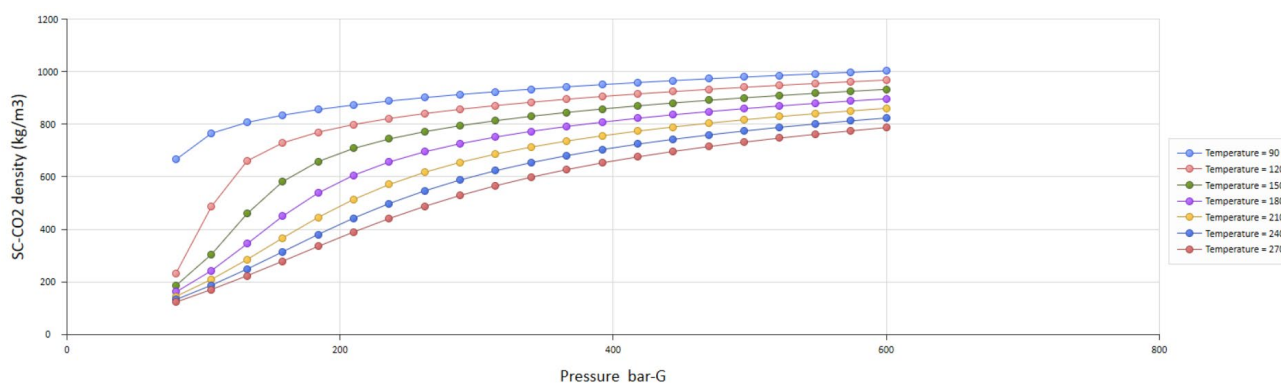

Figure 5: Predicted SC-CO_2 isotherms using BWRS

The parameters for Equation 3 should be handled with care. Literature values for hemp oil solubility are wide-ranging depending on SC-CO_2 use rates, raw material properties, and methods of determination. In general terms, higher densities improve solubility of hemp oil in the SC-CO_2 [11].

Flowsheet Development of the Full Extraction system

System Level Model Selection

Conceptually, the typical SC-CO_2 systems are straightforward from a process design standpoint. A predetermined mass of hemp material is loaded into an extraction chamber, sealed, and exposed to a continuous and steady flow of SC-CO_2. The SC-CO_2 exits the extraction chamber in an oil-rich state before oil is separated gravimetrically and CO_2 is evacuated. In larger systems, the CO_2 is recycled.

From a model standpoint, CHEMCAD offers various options on unit operations to suit the end user's ultimate objectives. The decisions for the end user are as follows:

1. Is a steady-state model acceptable for the specific evaluation?
2. What level of rigor is necessary for the modeling of individual unit operations involving SC-CO_2 mass transfer?
3. Will cannabinoid isolation be necessary in a system-level model?

The time-dependence of oil extraction in the typical SC-CO_2-hemp oil system description suggests that a dynamic model is most appropriate. Furthermore, it is advantageous to model total oil collected over time. CC-DYNAMICS and associated unit operations will be used to model the system.

The level of rigor in designing the system will be determined by end goals and the VLE options available in CC-NXT. Some of the key equilibrium-based separation steps in a SC-CO_2 system are as follows:

- Binary CO_2-water equilibrium in extractors, separators, or storage tanks
- Multicomponent CO_2-water-oil equilibrium in extractors and separators (or gravity separator)

Should the individual cannabinoid constituents need to be visible in a full extraction model, the same equilibrium steps apply. They are typically associated with the oil phase of the hemp material. The oil can then be analyzed for cannabinoid content on a biomass-free basis after extraction is complete.

Given the variety of possible equilibrium steps and potential complexity to evaluate each, a practical CC-NXT model was developed based on the following assumptions:

1. Extraction of oil from hemp biomass will require a custom unit operation based on CO_2-oil solubility models.
2. Modeling of cannabinoid separation from hemp biomass is not necessary if the goal is maximizing oil removal (as opposed to selective removal of cannabinoid from biomass AND oil).
3. Separation of oil from CO_2 can be simplified using a single CSEP unit operation, although in practice this can require multiple stages.
4. CO_2 will be recycled. Water and CO_2 will be separated by user preference in the same CSEP UnitOp. For this design, water is assumed to fully assimilate with the oil and not accumulate in the system. Doing so enables CC-NXT to accurately predict the pure component properties of SC-CO_2.
5. Any SC-CO_2 phase change steps should be modeled with pure CO_2, regardless of phase.

Using these assumptions, Figure 6 below illustrates the fully assembled system-level model.
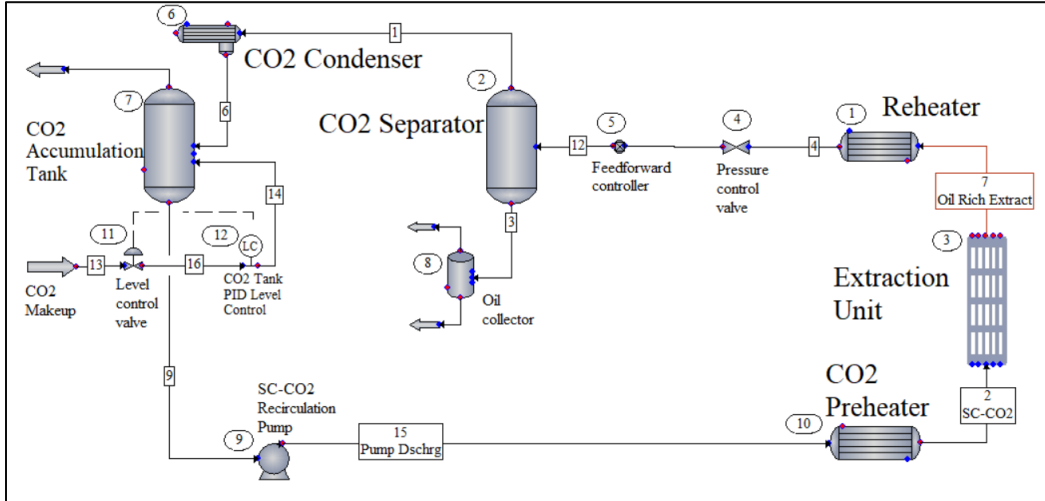
Figure 6: Separation of oil and supercritical CO₂ from biomass

For complete reference of the diagram, see Table 1 below.

Table 1: SC-CO$_2$ Extraction Flowsheet Unit Operation Legend		
UnitOp ID	**UnitOp Type**	**UnitOp Description**
1	Heat Exchanger	CO$_2$-oil mix reheater
2	Component Separator	Remove extracted oil and moisture from CO$_2$
3	Excel	Custom extraction unit
4	Valve	Back pressure valve
5	Controller (Feed-forward)	Controller to correctly set CO$_2$ temperature post-separator
6	Heat Exchanger	CO$_2$ condenser
7	Dynamic Vessel	CO$_2$ accumulation tank
8	Dynamic Vessel	Oil collector
9	Pump	Feed pump to extraction unit
10	Heat Exchanger	CO$_2$ preheater
11	Control Valve	Makeup-CO$_2$ control valve
12	PID Controller	CO$_2$ accumulation tank level controller

Hemp Component Parameters

The custom extraction operation above requires a means to aptly define the hemp. For modeling purposes, the user can establish that hemp is made up of biomass and the typical fatty acid profile observed in whole hemp, floral material, or seeds.

A typical hemp oil makeup would be as follows, according to Table 2 [8]:

Table 2: List of Typical Fatty Acids Found in Hemp Oil							
	Palmitic	Stearic	Oleic	Linoleic	γ-Linolenic	α-Linolenic	Eicosenoic	Behenic
Fat type	C16:0	C18:0	C18:1	C18:2	C18:3	C18:3	C20:1	C22:0
CAS No.	57-10-3	57-11-4	112-80-1	60-33-3	506-26-3	463-40-1	506-30-9	112-85-6
CHEMCAD ID	912	550	549	548	**	**	No	No
Composition Range (%)	5-6	1-2	10-12	55-60	3-4	17-19	0.6-0.9	0.1-0.3

** CC lists linolenic acid (ID 1529) with CAS 463-40-1

Table 2 lists eight unique fatty acids that make up the constituents of a typical hemp oil. It is conceivable that the user could create a single, custom oil component and regress parameters to suit the extraction unit shown in Figure 6. Because fatty acid component data is available in the CC-NXT database, the individual compound approach was taken. Eicosenoic and behenic acids are assumed to be zero, as they are low in concentration according to Table 2. Also, CC-NXT does not differentiate between the stereoisomers of the linolenic acids. There exists a relative volatility difference between the two, but the alpha stereoisomer content is approximately 5 times higher than the gamma. So, for the purposes of SC-CO_2 extraction, the single linolenic acid component provided in the CC-NXT database will suffice. Compositional data available unique to gamma or alpha linolenic acids are simplified to a single linolenic.

Although the oil is of primary interest, an undesired constituent representing the un-extractable fraction of the hemp shall be included. A simple, starchy, or fibrous user-created compound can be added using a heat capacity ranging from 0.2-0.5 Btu/lb-°F, a high melting point, and solid density. This component should also be listed as a solid. In CC-NXT, this is accomplished by navigating to the Thermophysical ribbon and clicking **Identify Solid Components**. After the minimum data is entered, the new component is named "Dead Biomass." The simulation composition of the hemp model, based on hemp seed, is represented below in Table 3:

Table 3: Initial Composition of Raw Hemp Seed Used in CHEMCAD NXT SC-CO_2 Extraction Simulation	
Constituent	**Mass Percentage**
Dead biomass	55%
Water	5%
Linoleic acid	22.8%
Linolenic acid	9.2%
Oleic Acid	4.8%
Palmitic Acid	2.4%
Stearic Acid	0.8%

It should be noted that cannabinoid isolation and simulation thereof is reserved in a separate CC-NXT model, to be discussed later in this paper. It is therefore unnecessary to list these as SC-CO_2 extraction components in Table 3.

Extraction Mass Transfer Model Selection

Plant-derived oil extractions using SC-CO_2 have been studied in depth over the years. It is understood that a) these plant oils possess intrinsic solubility limits within the solvent system, including SC-CO_2, and b) release from the biomass is mass-transfer limited. Mass-transfer model approaches, discussed in other works, include bulk desorption, diffusion, or a variable surface type, where solute surface position shrinks toward the center (often referred to as *shrinking core*).

An illustration of a typical dynamic pattern for SC-CO_2 is shown in Figure 7 below. There is an initial constant extraction rate (CER) period where the solvent is well mixed and in full contact with solute material. In this period, there is limited resistance due to mobilization of the solute across cell biomass. The equilibrium concentration is therefore limited only by solubility of the solute in solvent. This uniquely identifiable period shall be governed by SC-CO_2 properties generated by CC-NXT and applied by Equation 3. If the SC-CO_2 flow rate to the extraction unit remains constant, the overall extraction rate will follow the CER pattern in Figure 7.
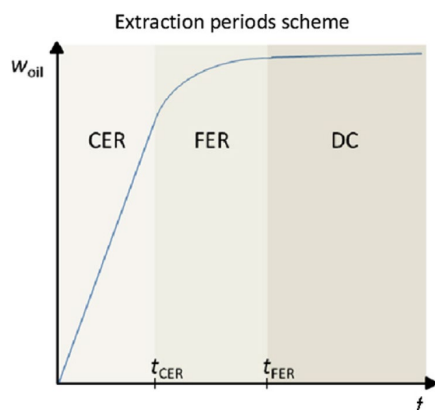
Figure 7: Typical plant oil extraction periods scheme using SC-CO2 [2]

The diminishing contribution of convective mass transfer between solute and solvent begins at a point t_{CER}, as seen in Figure 7. This period is referred to as the falling extraction rate (FER), where straight-line solubilities are no longer observed. The ability of the oil to coexist with the solvent is highly dependent on its ability to be released from the hemp biomass. Figure 7 also includes a third period, referred to as diffusion controlled (DC).

For practical modeling using a user-defined Extraction unit operation, it is necessary to separate post-CER phase from the solubility-limited initial period. Although some researchers choose to differentiate between a FER and DC period, it is also possible to combine the two into a uniform model, at a time t_{cer}. Recent developments in axial flow (upward flow of a solvent through a solute-rich packed bed) have led to a unified broken and intact cell (BIC) model. Rigorous BIC models attempt to differentiate between regions of plant cell material depending on solvent proximity to solute embedded closer to particle surface vs. the core location. Intact cells are controlled by internal mass-transfer resistance governed by typical diffusion models.

A combined FER/DC equilibrium equation is reported from literature as follows [9]:

$$c = k'_{FER} \frac{w_0}{Q_{CO_2}} e^{-k'_{FER}(t-t_c)} \qquad \text{Eq. 4}$$

where c is the concentration of the oil in the supercritical solvent, k'_{FER} is the extraction rate parameter in the falling/diffusion controlled period, w_0 is the initial mass of solute entering the falling/diffusion controlled period, Q_{CO2} is the volumetric flow rate of the CO_2 entering the extractor, t_c is t_{CER}, or the changeover time from the constant to falling/diffusion controlled period, and t is current time. It is expected that k'_{FER} can be temperature- and particle property-dependent, but will be held constant in this project.

Using Equations 3 and 4, a dynamic model can be incorporated into a spreadsheet for the custom unit operation in Figure 6. This sheet is described in the next section.

Data Mapping and Excel Calculation Extraction Sheet

A calculation sheet for the extraction unit features the following four sections within the same tab:

1. Inputs from CC-NXT
2. Inputs from the user (entered directly into the sheet)
3. Calculations
4. Outputs to CC-NXT

Inputs and outputs between the sheet and CC-NXT must be established using the Data Map feature. Inputs can include a variety of flowsheet data. For this model, CC-NXT will supply parameters of incoming SC-CO_2. As seen in Figure 6, CO_2 accumulation tank contents determine the initial concentrations as specified by the user. It is best that this should be pure CO_2, so that CC-NXT can more accurately estimate incoming density. These parameters include concentrations, temperature, density, pressure, and vapor fraction. CC-NXT inputs should also include the current dynamic time for reference during the run.

The user inputs section includes the initial charge data, parameters used for Equations 3 and 4, estimated water solubility in the SC-CO_2, time step used (typically 1 minute), and oil mass fraction where

the CER period ends. This specific mass fraction is not included in any of equations above, but it is observed at time t_{CER}. It is understood that t_{CER} can vary between batches, and the practical approach is to estimate this time based on a known rate limiting oil content. From Table 3, the initial oil content is 40%. For the simulation, the oil content at the end of the CER period will be 10%. User input values for the extraction unit are summarized below:

Table 4: User Input Values for Custom SC-CO_2 Extraction Unit Operation in CHEMCAD-NXT	
Parameter	**Value**
Initial Charge (kg)	100
Mass Fractions	**Table 3
Water Solubility in SC-CO_2 (mg/kg)	3
Relative Step size (min)	1
Solubility Parameters for Eqn. 3	
a (K)	-3131.7
b	-43.495
k	7.2812
Diffusion Calc. Parameters for Eqn. 4	
k'_{FER} (min^{-1})	0.02
Oil Diffusion-Limited mass fraction	0.1

A calculation section follows to collect all data, adjust accordingly, and compute necessary results for output at the current simulation time. All input concentrations are normalized to ensure that the sum of all fractions is equal to 1. Next, total oil content remaining at t_{CER} is calculated. Oil content, for this simulation, is the sum of all fatty acid constituents.

Results from Equations 3 and 4 are updated throughout the dynamic run. However, the next set of calculations requires monitoring of current run time and its relative proximity to the unknown t_{CER}. To accomplish this, a continuously run subroutine needs to be set up in the sheet background to monitor dynamic time. At each dynamic time step, new calculations can be made. A worksheet change event in the VBA Project section of the Excel workbook following the syntax expression.**Change** (Target) is applied in the Microsoft Excel Objects tree of the VBA Editor. The purpose is to monitor each time CC-NXT changes the dynamic time in the Inputs section of the spreadsheet. After Excel detects a change in dynamic time, it will update those values that are dependent on time. For more details, consult Microsoft Office Excel Worksheet Object help documentation.

Outgoing oil content is calculated following either Equation 3 or 4, again depending on t_{CER}. For ease of calculations, the individual fatty acid contents, in g/L, are calculated by multiplying fatty acid fraction of total oil by total estimated oil content. For example:

Outgoing linoleic acid concentration, c_{out} (g/L) = $x_{linoleic\ acid}$ /x_{oil} * c_{oil} (from Eqn. 3 or 4).

This assumes equal distribution of fatty acids in the initial hemp charge, as well as their affinity to the SC-CO_2. At any step change, residual fatty acid content is then calculated as follows:

$$m_{t+1} = m_t - \frac{w_{CO_2}}{\rho_{CO_2}}(c_{out} - c_{in})\Delta t \text{ for any fatty acid at dynamic time t+1} \qquad \text{Eqn. 5}$$

where m is residual fatty acid mass, w_{CO_2} is the mass flow rate of CO_2 exiting the extraction unit, ρ is the SC-CO_2 density, c_{out} is equilibrium fatty acid content, and Δt is the unit time step change.

As run time progresses, fatty acid content reduces accordingly with Equation 5. The calculation section in the spreadsheet includes a cell reserved for checking overall oil content at time t+1 to verify if the FER/DC periods have been entered. If they have, that current time t is reserved as the fixed t_{CER} used in Equation 4. The simulation proceeds using Equation 4 to estimate equilibrium oil content.

Global Thermodynamic Model Selection

The BWRS K-model has shown accuracy for fluid behavior in the supercritical region, including gas mixtures [6]. As discussed earlier, the BWRS EOS sufficiently estimates properties of the pure SC-CO_2. However, the flowsheet contains several unit operations where CO_2 is in a subcritical state and true VLE estimates are necessary. It is advantageous to define which VLE-based unit operation can contain mostly or all CO_2. From Figure 6, those unit operations are 6, 7, 9, 10, and 11. The oil extraction unit relies on the aforementioned separation models, and can thus be disregarded in this evaluation. As a general rule, a system operating above the critical temperature with a miscible liquid phase can use an EOS model without binary interaction parameters (BIPs). There is an assumed single species in both phases, therefore BWRS was selected.

Dynamic Run Results

After ensuring all settings for each of the unit operations in Table 1 are suitable for the simulation, the run-time parameters are entered. For the dynamic run settings, all streams and UnitOps should be recorded. This is set up under the Dynamic section of the Home ribbon; click the **Set Run Time** drop-down to access the **Record Streams** and **Record UnitOps** dialogs. Use the **Set Run Time** command itself to set the appropriate step size and run time. For this demonstration, 1-minute steps and 140 minutes will be sufficient.

The hemp extraction unit charge conditions described in Table 4 are established, as well as dynamic vessel charge conditions. The CO_2 accumulation tank (UnitOp 7) is charged with 1000 kg of pure CO_2 initially. Other parameters should be adjusted as shown in Table 5:

Table 5: Unit Operation Parameters for SC-CO_2 Extraction System	
Simulation Parameter	Value
SC-CO_2 flow through system (set in CO_2 accumulation tank, UnitOp 7)	40 kg/min
UnitOp 10 (CO_2 preheater) outlet temperature	122 °F
UnitOp 9 (CO_2 pump) outlet pressure	300 bar (gauge)
UnitOp 4 (pressure control valve) outlet pressure	40 bar (gauge)
UnitOp 12 (level control) set point (optional, depending on venting potential)	1500 kg
UnitOp 6 (CO_2 condenser) outlet temperature	24 °F

Clicking **Run from Initial State** will begin the dynamic execution and calling of the simulation data maps. A stream box can be created under the Drawing ribbon and placed in the flowsheet. As this is a dynamic simulation, the values displayed in the stream box will change over the course of the dynamic run. For comparison, see time-dependent results shown in Tables 6 and 7.

Table 6: Dynamic Simulation Results at t = 30 minutes

Stream No.	15	2	4	12	1	3	6	13
Name	Pump Dschrg	SC-CO2	Oil+SC-CO2	Low P Extrct	CO2 Vapor	Recvrd Extrc	CO2 Condnsd	Makeup CO2
- - Overall - -								
Temp F	54.75	122.00	90.00	44.59	44.59	80.00	24.00	77.89
Pres bar-G	300.00	300.00	300.00	40.00	40.00	40.00	40.00	400.00
Enth MMBtu/min	-0.34979	-0.34715	-0.35228	-0.35228	-0.34202	-0.0030679	-0.35109	-0.029642
Mass flow kg/min	40.00	40.00	40.98	40.98	40.00	0.98	40.00	3.40
Flow rates in kg/min								
Carbon Dioxide	40.00	40.00	40.00	40.00	40.00	0.00	40.00	3.40
Water	0.00	0.00	0.12	0.12	0.00	0.12	0.00	0.00
Linolenic Acid	0.00	0.00	0.20	0.20	0.00	0.20	0.00	0.00
Linoleic Acid	0.00	0.00	0.49	0.49	0.00	0.49	0.00	0.00
Oleic Acid	0.00	0.00	0.10	0.10	0.00	0.10	0.00	0.00
dead biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palmitic Acid	0.00	0.00	0.05	0.05	0.00	0.05	0.00	0.00
Stearic Acid	0.00	0.00	0.02	0.02	0.00	0.02	0.00	0.00

Table 7: Dynamic Simulation Results at t = 60 minutes

Stream No.	15	2	4	12	1	3	6	13
Name	Pump Dschrg	SC-CO2	Oil+SC-CO2	Low P Extrct	CO2 Vapor	Recvrd Extrc	CO2 Condnsd	Makeup CO2
- - Overall - -								
Temp F	53.38	122.00	90.00	43.90	43.90	80.00	24.00	77.89
Pres bar-G	300.00	300.00	300.00	40.00	40.00	40.00	40.00	400.00
Enth MMBtu/min	-0.34984	-0.34715	-0.34862	-0.34862	-0.34205	-0.00019019	-0.35109	-0.023298
Mass flow kg/min	40.00	40.00	40.09	40.09	40.00	0.09	40.00	2.67
Flow rates in kg/min								
Carbon Dioxide	40.00	40.00	40.00	40.00	40.00	0.00	40.00	2.67
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Linolenic Acid	0.00	0.00	0.02	0.02	0.00	0.02	0.00	0.00
Linoleic Acid	0.00	0.00	0.05	0.05	0.00	0.05	0.00	0.00
Oleic Acid	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00
dead biomass	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Palmitic Acid	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00
Stearic Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

As all streams and UnitOps were recorded, the time-stamped data can be trended or exported accordingly. The extraction unit model was set up to partition the extraction rates into two phases (CER and FER/DC), and such data should reflect this. To inspect the fatty acid flow trends, use the **Charts** drop-down menu from the Home ribbon. Clicking **Stream History** will permit the selection of stream information to be plotted over the course of the simulation.

The Dynamic Stream Chart Options dialog allows the selection of specific components, as well as the Mass option to display composition by total mass. Stream 4 is of particular interest, as this is the oil-rich stream exiting the extraction unit prior to any other separations. Keeping in mind that the fatty acid removal rates are proportional to the original mass fractions, a plot for each is shown in Figure 8:
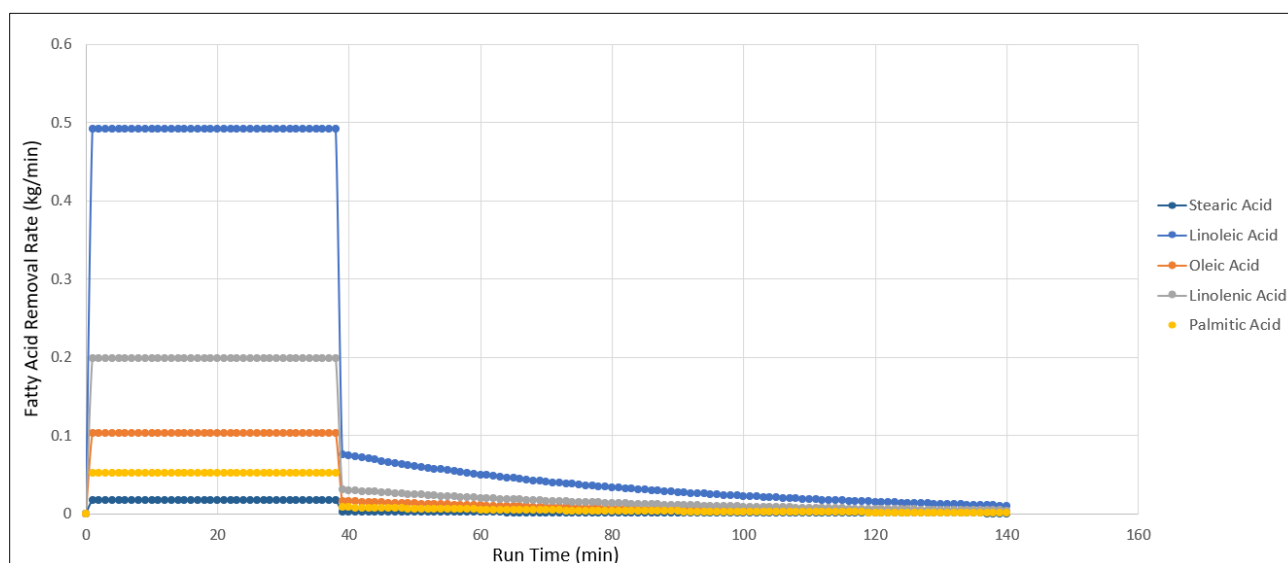
Figure 8: Fatty acid removal rates from an initial 100 kg charge of hemp biomass using 40 kg/min supercritical CO_2 solvent at 300 bar and 122 °F

The total extracted material collected in UnitOp 8 (oil collector) can also be plotted over time. This is the total of all fatty acids and moisture after the CO_2 has been removed. See Figure 9 below:
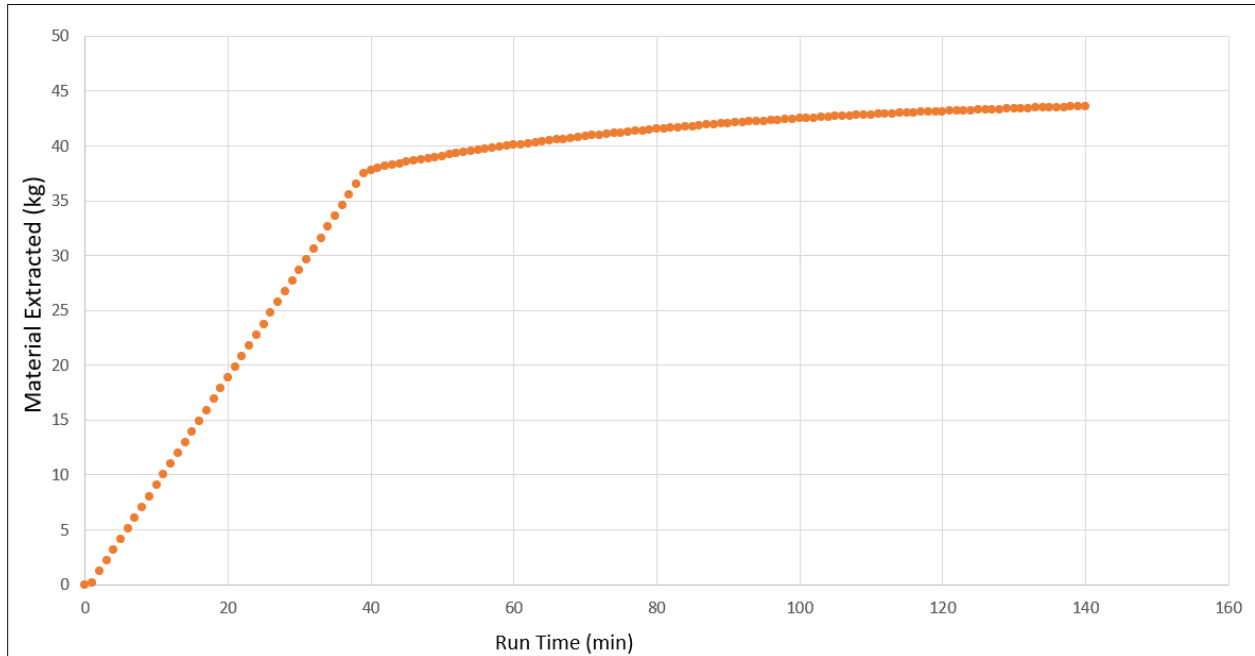
Figure 9: Total extracted material from an initial 100 kg charge of hemp biomass
using 40 kg/min supercritical CO_2 solvent at 300 bar and 122 °F

To find the total mass at the end of 140 minutes, the roll-up plot (live plot during a dynamic run) can be inspected. Alternatively, this value can be found from a report for UnitOp 8 (oil collector). From the Home ribbon, click **Reports** > **Batch Results**. In this simulation, the value is 43.7063 kg. Comparison of the curve shape from Figure 9 with Figure 7 highlights the model incongruity between a CER and FER/DC period. In practical terms, the model-predicted value of total extracted material will come relatively close to the real value over the course of a run. It should also be pointed out that the total extracted material in Figure 9 includes moisture.

Modifying temperature or pressure of the SC-CO_2 also can impact the removal rates shown in Figures 8 and 9. Should there be interest in operating at different pump discharge pressures, this will have an impact on the predicted density values in Figure 5. As an example, this can be reduced from 300 bar to 200 bar. CC-NXT predicts a lower SC-CO_2 density and therefore lower oil solubility in the system. Figure 10 below illustrates the simulation results of lowering the pressure:
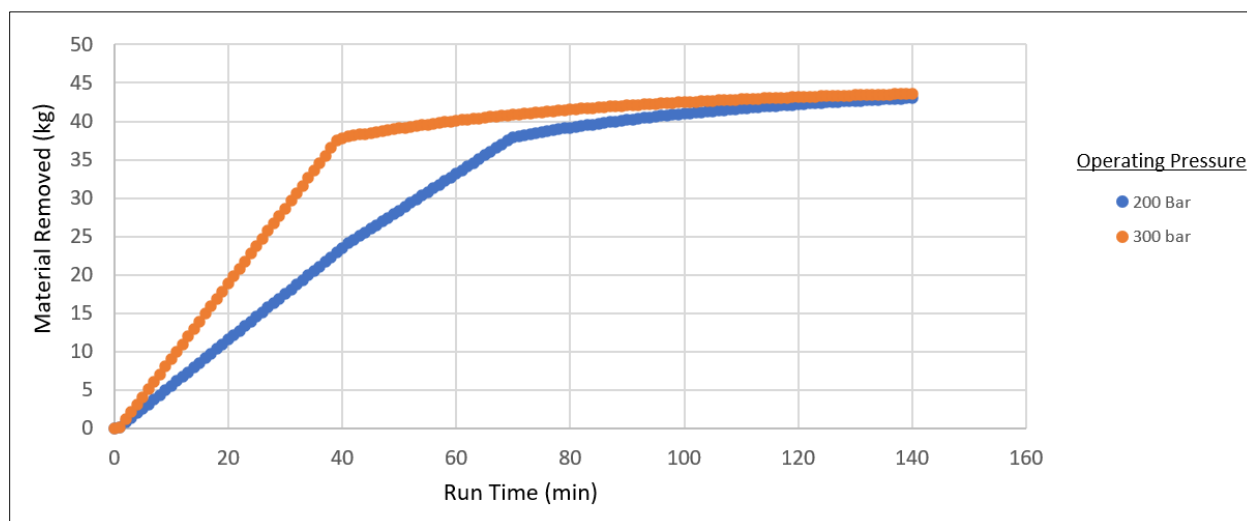
*Figure 10: Total extracted material from an initial 100 kg charge of hemp biomass
using 40 kg/min supercritical CO_2 solvent at varying pressures and 122 °F*

As seen in Figure 10, the lower density that results from a reduction to 200 bar delays the extraction time, particularly in the CER phase. It can be observed that the masses removed from the two run cases will increasingly be closer as time progresses. Similar comparisons can be made at other temperatures, pressures, and SC-CO_2 flow rates.

Isolation of cannabinoid constituents from hemp oil

The second part of the hemp oil application is separation of the higher-value components from the oil base. The oil may be filtered or winterized, followed by further purification techniques. One such purification technique is the fractional distillation method. The CC-BATCH module permits modeling of such fractional techniques and simulates separation of the unique components. One of the persisting issues is the separation of THC from CBD. CC-NXT does not include these components in the database, but it does allow for creation of new components.

Creation of UNIFAC-based Compounds

For demonstration, four cannabinoids are chosen to be added to the component database. In addition to CBD and THC, CBG and CBN are included for the evaluation. Physical property information about the component is helpful, but not required. The basic steps to add the new components are as follows:

1. Navigate to the Component Database ribbon and click **New** under the User Components section.
2. Enter a name for the new component.
3. Enter a normal boiling point.
4. Enter the correlation method (UNIFAC group contribution method for this project).
5. Enter group data for the component.

Four new names and CAS codes are added. Boiling points for cannabinoids are typically very high at atmospheric pressure. There are various sources for normal boiling points, and at high levels, predictive methods may be required. For this project, the Percepta software from ACD/Labs was used (via ChemSpider) to estimate normal boiling points.

Finally, the UNIFAC group contribution method is used for correlation. To define the compound, each of the carbon atoms needs to be matched with specific subgroups. Table 8 shows subgroup allocations used for the cannabinoids in this system.

Table 8: UNIFAC subgroup assignments for key cannabinoid components				
	CBD	CBG	CBN	THC
CAS Number	13956-29-1	25654-31-3	521-35-7	1972-08-3
Boiling Point (°F)	877.82	878.72	889.7	734.72
Groups				
Non-Ring				
CH3-	3	4	2	3
CH2<	3	5	4	4
CH2=C	1			
CH=C	1	2		1
Ring				
RCH2<	2			2
>RCH-	2			2
>RC<	1			
ACH	2	2	5	2
AC-	1		4	2
ACCH3			1	
ACCH2	1	2	1	1
Oxygen				
ACOH	2	1	1	1
CH-O			1	1

The addition of THC and CBN is limited by the lack of the specific UNIFAC ether group in the construction of the compound. To circumvent this, contribution of an ether with an extra hydrogen was selected as an alternative that is similar in structure. To maintain consistency in molecular weights, the extra hydrogen had to be removed elsewhere, and one of the hydrogens from a methyl group was eliminated. For illustration, the modified structure of THC that matches the subgroup locations in Table 8 is shown in Figure 11 below.
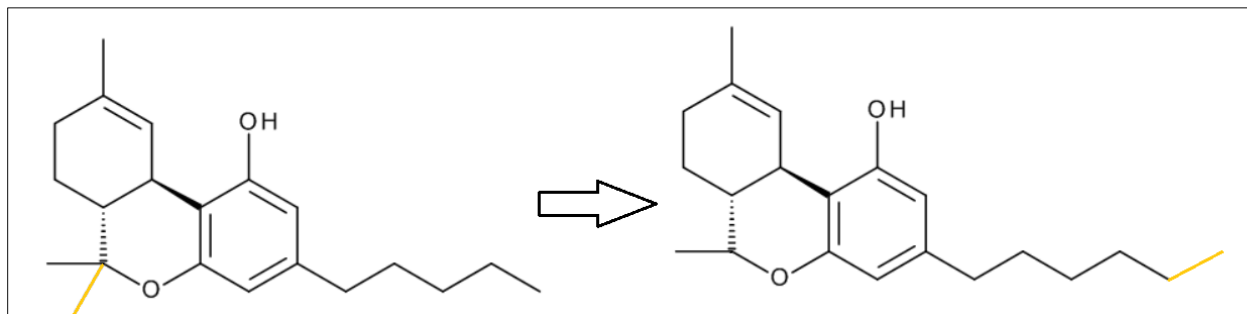
Figure 11: Molecular alteration of THC to accommodate UNIFAC subgroup availability

All significant functional groups are still present in the modification. Any interactions with other components in the mixture would be expected to be similar. For CBN, the same modification was made.

Once the compounds are entered, CC-NXT performs predictions of several properties such as critical points, heat capacities, and latent heats. The user then can review these parameters and adjust accordingly. For this project, cannabinoid melting point predictions are replaced with literature values [7].

Construction of Hemp Oil/Cannabinoid System

For ease of simulation and alignment with scope, the SC-CO₂ extraction system was set up for oil/fatty acid removal only. It is possible to add cannabinoids to the system if the solubility and diffusion data are available. For this system, cannabinoid content is a small fraction of the overall oil content, so it was excluded from the extraction model. Because the batch distillation simulation is a separate operation from the extraction, the desired cannabinoid content is added back based on the user's preference.

The extracted material from the SC-CO₂ simulation includes fatty acids and water only. The moisture can be included if preferred, as it was added to the final collector for convenience. There is typically a 300-400 degree difference in water and hemp oil boiling points. Accounting for boiling point elevation of water, it will most likely be the first component removed in a distillation. The operating pressure will be modeled as a vacuum system at very low conditions. Residual moisture is likely flashed during air evacuation of the system. At very low pressures (under 0.1 mbar absolute) and with the moisture quantity in the hemp charge (5 kg), this would be expected, particularly if moderate heat is applied at startup. For practical purposes in this batch distillation evaluation, moisture will be excluded. Note that it can be added easily if the effect of moisture on cannabinoid separation is of interest.

During the SC-CO₂ extraction evaluation, the K-value method was set to BWRS. In the case of oil distillation, this setting is no longer valid. In this system, multicomponent vapor-liquid parameters are unknown for the cannabinoids and would otherwise use activity coefficient models to predict the separations. For cannabinoids, these BIPs are generally unavailable unless provided through laboratory evaluations. It is therefore best to use UNIFAC for VLE predictions. As mentioned above, water is excluded from the system; if water is to be included in the charge data, care should be taken when

interpreting results. While CC-NXT does include a UNIFAC subgroup for H_2O, the water/hemp oil phases may not be completely miscible. UNIFAC VLE would not be suitable in this scenario.

A potential issue for oil processors is a high concentration limit of THC being exceeded in the oil. For this exercise, the scope is to concentrate the CBD while removing THC. The initial oil is assumed to have higher THC than desired. Using the data from the runs above, the estimates for the extracted content remaining in the oil collector are shown in Table 9. Note that moisture was excluded.

Table 9: Total Hemp Oil Composition to Be Charged to Batch Distillation System		
	Total Mass (kg)	Total Mass Percent (%)
Linoleic Acid	21.951	54.14
Linolenic Acid	8.857	21.84
Oleic Acid	4.817	11.88
Palmitic Acid	2.311	5.70
Stearic Acid	0.770	1.90
Water	0	0
Cannabidiol (CBD)	1.5	3.70
Delta-9-tetrahydrocannainol (THC)	0.3	0.74
Cannabinol (CBN)	0.02	0.05
Cannabigerol (CBG)	0.02	0.05

Batch Distillation Model Parameters

The batch system for this evaluation will be modeled as a single-stage (not including total condenser) distillation with reboiler. The flowsheet should include a batch distillation unit operation, two batch tanks, and a stream reference (for still charge data). The two tanks are used for distillate and residual oil collection. The goal is to reduce the hemp oil THC content from 0.74% as shown in Table 9 to below 0.28% while concentrating CBD. This CBD concentrate will be collected at the bottoms, while the distillate contains the THC-enriched fraction. The batch distillation simulation flowsheet is shown in Figure 12.
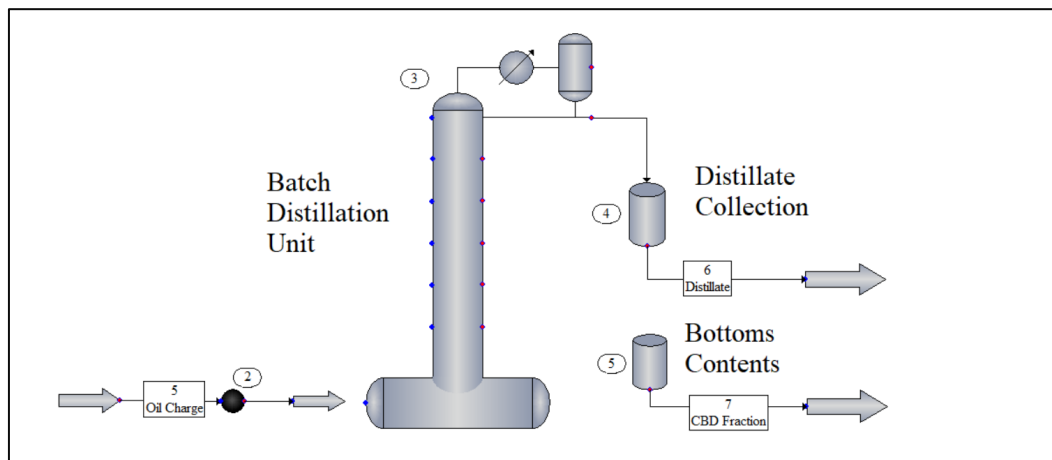
Figure 12: Batch distillation and purification of hemp oil components

Double-clicking the batch distillation unit calls up a list of parameter categories required for specification. Pot charge specification can be done here, but is not necessary in this case. The pot charge data will be collected from stream 5 and the stream reference (UnitOp 2) shown in Figure 12. The batch column set of parameters includes those that are unique and will not be modified from step to step. This includes number of stages, condenser type, holdup volumes, and efficiencies. For this system, only two stages are necessary, with one operational step. The condenser is a total condenser. Pressure is specified here at 0.06 mbar. Residual or final holdup is transferred to tank ID 5, as shown in Figure 12.

The operational parameters indicate how each step will be operated. In this project, only the one step requires such specification. The first specification used is reflux ratio, which is set to a low reflux value of 0.01. No deliberate refluxing is necessary, but an assumed value is placed here to reflect potential heat losses from the vapor to the still surface prior to being condensed. Reboiler duty is also specified here at 10,000 Btu/hr (0.01 MMBtu/hr).

There are several options available for identifying when the run is complete. A fixed time is a convenient and simple method that generally provides results that converge. However, because the goal is to purify the CBD-rich fraction until the THC has been reduced to 0.28%, the stop option is set to stop when the bottom mass fraction reaches 0.0028. Given that a long step size may result in overconcentration of the CBD fraction (and stopping well below 0.28% THC), the step size is set to a relatively low value of 0.0167 hour, or 60 seconds. No additional settings are required in this dialog. No other sections within the Batch Distillation menu require specification except the user's preferred chart options.

Batch Distillation Run Time Results

After all charge data is entered, exit the Batch Distillation menu and click **Run All** on the Home ribbon. From Table 9, the stream reference UnitOp will load stream data into the batch distillation unit prior to the calculation sequence. The more volatile fatty acids will boil off first, followed by some fractions of cannabinoids. The run time progresses based on residual THC in the bottom. For the set of conditions in this project, the total run time is 1.35 hours (81 minutes). Table 10 summarizes the resulting run data.

Table 10: Simulation Results of Batch Distillation and Purification of Hemp Oil Components

Stream No.	5	6	7
Name	Oil Charge	Distillate	CBD Fraction
- - Overall - -			
Temp F	90.000	260.101	281.607
Pres mbar	1013.530	0.060	0.060
Enth MMBtu/batch	-0.088836	-0.077000	-0.0040638
Mass flow kg/batch	40.546	38.299	2.247
Component mass %			
Linoleic Acid	54.14	56.66	11.12
Linolenic Acid	21.84	22.41	12.18
Oleic Acid	11.88	12.30	4.78
Palmitic Acid	5.70	5.86	2.93
Stearic Acid	1.90	1.75	4.38
Water	0.00	0.00	0.00
Cannabidiol	3.70	0.24	62.67
delta-9-THC	0.74	0.77	0.28
Cannabinol	0.05	0.00	0.82
Cannabigerol	0.05	0.00	0.86

The simulation was able to terminate at a THC percentage of 0.28%, at which point the CBD concentration had reached 62.67%. For batch distillation run data options, navigate to the Home ribbon and click **Charts** > **Batch Column**. Here the user can choose to plot mass fractions of the bottoms content, and select components to include in the chart. The cannabinoid fractions are plotted here. On the Chart ribbon, the **Export Chart** drop-down list includes an option to export the chart data as a .csv file directly to Excel. Additional customization of the residual cannabinoid chart in Excel is shown in Figure 13 below. Judging from the results, the CBD content rapidly rises when the batch nears the end. It likely would require very little time to extend the batch and concentrate further. To monitor, distillate temperature is plotted and shown in Figure 14. This data enables the user to anticipate the proper distillate temperature when the desired CBD concentration is reached in the bottoms. Should there be interest in concentrating higher, the run time would need to be extended. Either the stop criteria can be modified to distill to a higher CBD content, or a projection can be made by visual inspection of the existing run data.

The distillate component mass values were also plotted over the course of the run and shown in Figure 15. The fatty acids make up the largest fraction, and were the only components selected in the chart. Upon observation, it is noted that individual fatty acid evaporation rates are constant throughout the run.
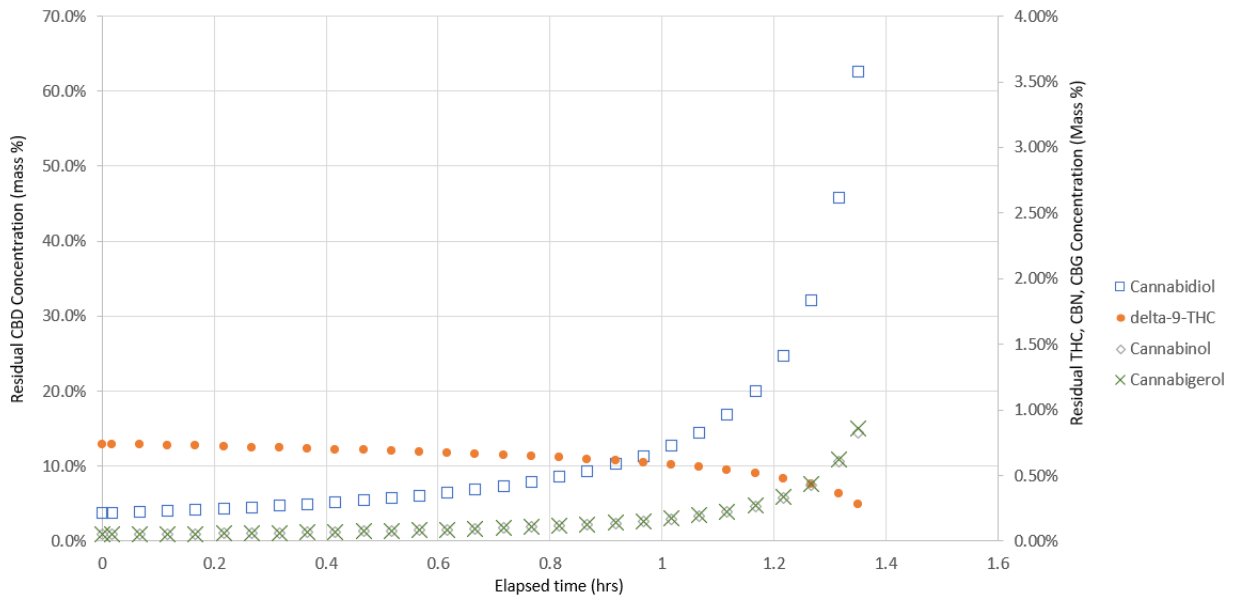
Figure 13: Residual cannabinoid concentration remaining from simulated batch distillation operating at 0.06 mbar predicted by UNIFAC
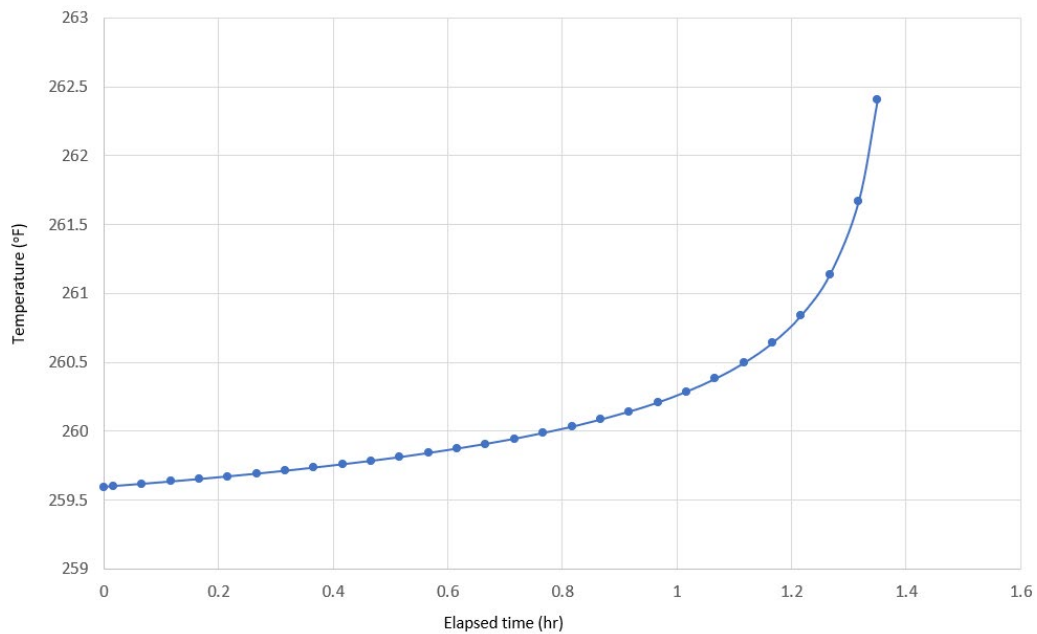

Figure 14: Temperature trend of hemp oil distillate from simulated batch distillation operating at 0.06 mbar predicted by UNIFAC
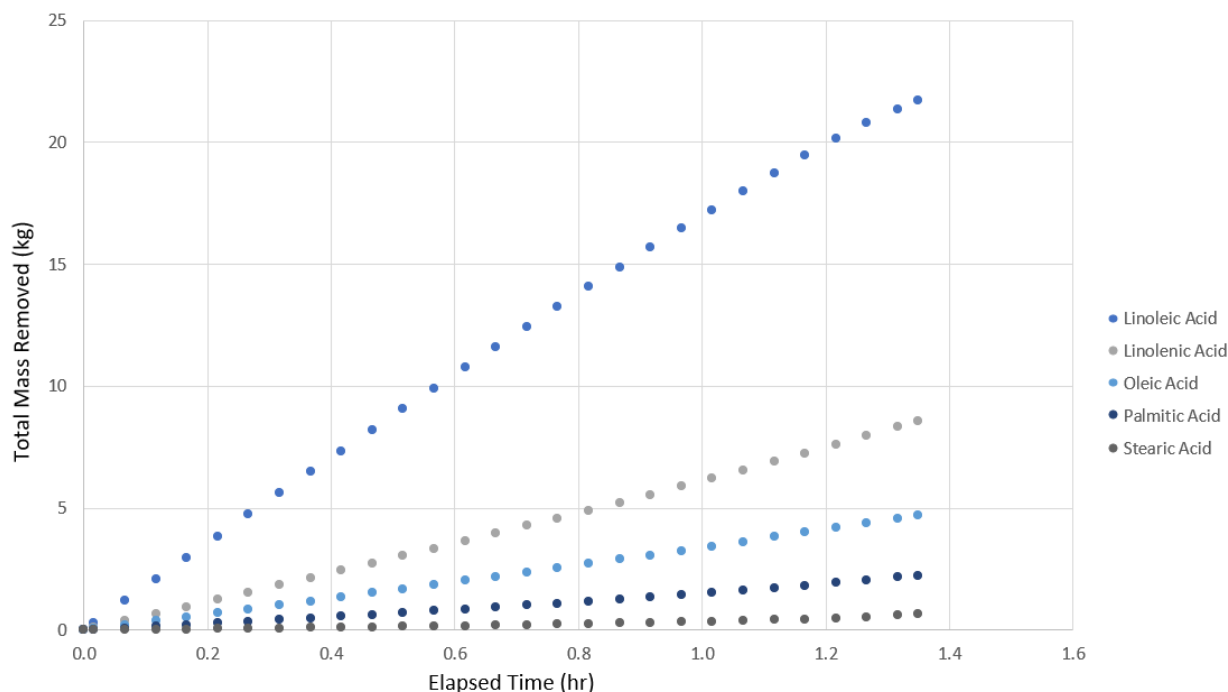
Figure 15: Cumulative fatty acids removed from hemp oil in simulated batch distillation operating at 0.06 mbar predicted by UNIFAC

Final Considerations

For the batch distillation system, the mixture is assumed miscible with no ternary or quaternary azeotropes present. Binary interaction parameters estimated from UNIFAC VLE can provide reasonable initial estimates for hydrocarbons, and by extension, organic compounds. The results from the simulations do not replace representative laboratory data to substantiate. It is therefore not recommended to design a system using compositions from UNIFAC-based simulations only. However, actual regression of lab data with CC-NXT offers very compelling results.

CC-NXT provides a meaningful and practical engine for simulation of standard and custom process operations. This hemp oil demonstration is one that can be adjusted to include other components or oil profiles. Additional cannabinoids, as well as the terpenes naturally present in the hemp biomass, can be added to the oil for additional simulations. This project can also be modified to evaluate similar extractions, not necessarily using SC-CO_2. With dynamic features, the ability to customize the extraction, and downstream simulation capabilities, CC-NXT is well suited for a variety of applications.

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