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# 1 Phenomenological Modeling and Intensification of 2 Texturing/Grinding-assisted Solvent Oil Extraction; 3 Case of Date Seeds (*Phoenix Dactylifera* L.)

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## 13 Abstract

14 ASE (Accelerated Solvent Extraction) and DM (Dynamic Maceration) were used with n-  
15 hexane to study the extraction of oil from date seed powders with different particle sizes.  
16 The intensification was studied with instant controlled pressure drop (DIC) as texturing  
17 pretreatment. DM yields increased from 4.57% to 10.49±0.05% dry-dry basis (ddb) when  
18 particle size decreased from 1.4 to 0.2 mm. For coarsely grounded seed powder, ASE oil  
19 yields were 11.35±0.05% ddb and 14.15% ddb for untreated and DIC date-seeds,  
20 respectively. Optimized DIC pretreatment allowed the smallest particle size powder to get  
21 15.2±0.05% ddb as ASE yields, whilst the 2-h DM yields increased from 4.67 to 11.62±0.05%  
22 ddb for particle size decreasing from 1.4 to 0.2 mm, respectively. Fundamental analysis of  
23 various powders was achieved through washing-diffusion phenomenological model. DIC  
24 texturing implied higher washing stage, with relative starting accessibility  $\% \delta Y_s$  of 70%  
25 against 55% for untreated particles. Consequently, the diffusion stage time was dramatically  
26 reduced, without great modification of effective diffusivity  $D_{eff}$  value. Therefore, DIC ground  
27 seeds greatly enhanced the mass transfer mechanism. The evaluation of starting accessibility

28  $\delta Y_s$  enables to establish an empirical relationship between  $\delta Y_s$  and particle diameter  
29  $\delta Y_s = f(D)$ . Finally, DIC texturing did not imply any modification of the lipid profile.

30 **Key words:** date seed oil, solvent extraction kinetics, DIC, particle size, Process  
31 intensification.

## 32 **1 Introduction**

### 33 **1.1 State of art**

34 Date palm, with a botanical name that probably derived from Phoenician as *Phoenix*  
35 *dactylifera*.L., belongs to the family of *Palmaceae* with about 235 genres and 400 species  
36 (Munier 1973). Date palm is a tree of arid and semi-arid native hot and humid countries but  
37 it has a wide capacity of adaptation. It is mainly located in northern Africa and the Middle  
38 East as well as west Asia and United States. According to the Food and Agriculture  
39 Organization of the United Nations (FAO 2010), the annual world production of date is  
40 estimated at 7 million tons (MT), from which seeds represent about 1 million tons.

41 Tunisia is one of the main date producers with about 125 000 tons/years with 60% of  
42 “Deglet Nour” variety (Rhouma 1993). Hence around 17 5000 tons of date seeds could be  
43 recovered and used as by-products thanks to their content of fatty acid, protein and high  
44 dietary fiber (Besbes, Blecker et al. 2004).

45 Nowadays date seeds are barely used for animal feeding and generally thrown away.  
46 The losses usually are higher than 30% of the whole production, which represents a huge  
47 tonnage near to 8 700 tons/year of date seeds in Tunisia (Borchani, Besbes et al. 2010). It is  
48 important to note that date seed plays an important part in date advantages. It contains  
49 more oil than date flesh, with some nutrient compounds (Al-Qarawi, Ali et al. 2003, Briones,  
50 Serrano et al. 2011, Aris, Norhuda et al. 2013). Indeed, date seeds contain between 5–12 g  
51 of oil/100g db (dry basis) whereas date flesh does not exceed 0.5% db of oil depending on  
52 the raw material composition and processing conditions (Al-Hooti, Sidhu et al. 1997,  
53 Hamada, Hashim et al. 2002, Besbes, Blecker et al. 2005, Habib and Ibrahim 2008).

54 It has been reported that date seed oil are composed of about 44% of saturated fatty  
55 acids, 41% of monounsaturated fatty acids and 14% of polyunsaturated fatty acid (Besbes,  
56 Blecker et al. 2004). The common composition of fatty acids is characterized by the presence

57 of four main compounds including oleic acid (41-50%), linoleic acid (12-19%), lauric acid (10-  
58 15%), and palmitic acid (10-11%) (Besbes, Blecker et al. 2004, Rahman, Kasapis et al. 2007,  
59 Nehdi, Omri et al. 2010, Aris, Norhuda et al. 2013); Oleic acid is reported to be used as a  
60 good anti-inflammatory drug and has fundamental role in cardiovascular diseases  
61 prevention (Larrucea, Arellano et al. 2001); while lauric acid has various medicinal,  
62 therapeutic (antibiotic and antiviral effects), and nutritional virtues (Desbois 2012).  
63 Furthermore, (Devshony, Eteshola et al. 1992) has proved that linoleic acid of date seed oil  
64 had good potential as cosmetic products. Since date seeds are rich in extractible  
65 components, they are regarded as real potentially economic source once they are valorized.

66 The main issue in developing date seed valuing is strictly correlated to oil extraction  
67 limits, in the main part from the hardness and compactness of its matrix. Thus press process  
68 for oil extraction is difficult to apply. Moreover, since the oil content is quite low, solvent  
69 extraction remains the only appropriate tool for this type of material. However, the most  
70 conventional solvent extraction technologies such as maceration require high solvent  
71 consumption and long extraction time (Besbes, Blecker et al. 2005). The main issue in this  
72 case is the slow diffusion of solvent and solute through the solid and the core successively  
73 (Allaf, Besombes et al. 2011). One of the most famous solutions was the use of super or sub-  
74 critical fluids as non-conventional solvents (Aris, Norhuda et al. 2013). Other very effective  
75 solutions have concerned some pretreatments such as grinding or texturing. Besides, the  
76 efficiency of solvent processes can be enhanced with ultrasound (Pan, Qu et al. 2011),  
77 microwaves (Chemat and Cravotto 2013), accelerated solvent extraction, etc. However these  
78 treatments trigger technical difficulties at industrial level and/or economic constraints. Thus,  
79 these operations were only successfully conducted at laboratory or pilot scales. Thus,  
80 scientists are attempting to adapt extraction processes to meet these strategic  
81 requirements.

82 Instant Controlled drop pressure (DIC) treatment is used for texturing. Since DIC  
83 treatment involves a high temperature short-time treatment of the product followed by an  
84 'instant' decompression towards a vacuum (Ben Amor and Allaf 2009, Allaf and Allaf 2014), it  
85 frequently results in controlled expansion, and allows the modification of the matrix  
86 microstructure. Thus technological abilities of DIC-treated plants are usually improved vis-à-

87 vis the solid-liquid interaction.. It can also preserve the molecular profile, even for heat-  
88 sensitive compounds.

## 89 **1.2 Fundamental (kinetic modeling)**

90 The fundamental phenomenological study of solvent extraction process was achieved  
91 through the two-stage kinetic model, which implies both “washing stage” (solvent/exchange  
92 surface interaction) and “effective diffusion” within the matrix. This allows identifying the  
93 limiting phenomenon and advising adequate technological solutions. Enhancements can  
94 then be divulged through the starting accessibility and effective diffusivity (Allaf, Zougali et  
95 al. 2014).

96 The intensification of solvent extraction is usually firstly performed by increasing the  
97 external interaction between solvent and solid surface (washing) triggering the solute on the  
98 surface removal. The amount of solute able to be extracted  $m_s$  depends on the nature of  
99 solvent and desired solute, the exchange surface, and the temperature. The extraction rate  
100 of solute extracted from the surface can be revealed by the following equation:

$$\frac{dm_s}{dt} = KS(w_{sat} - w_{solv}) \quad Eq. 1$$

101 Where:

102  $m_s$  is the masse of solute (kg of solute);

103  $K$ : is the solvent mass convection rate (kg of solvent  $m^{-2} s^{-1}$ ) depending on the stirring  
104 velocity and temperature.

105  $S$ : is the exchange surface area ( $m^2$ ) between the solvent and the solid; Normally  
106 affected by grinding;

107  $w_{sat}$ : is the dissolving coefficient at equilibrium (kg of solute per kg of solvent);

108  $w_{solv}$ : is the solute dissolved in the bulk solvent (kg of solute per kg of solvent).

109 The density of solute from the surface per unit of dry matter

$$\frac{dY_s}{dt} = KS_u(w_{sat} - w_{solv}) \quad Eq. 2$$

110 Where  $S_u$  is the specific interaction surface related to 1 kg of dry basis.

111 Where  $Y_s$  is the density per unit of dry matter of solute extracted by interaction  
112 between the solvent and the surface of the product (kg of solute per kg of dry matter or %  
113 db).

114 This stage of extraction process can be enhanced by:

- 115 • Agitation/stirring implying more solvent convection, which increases the value  
116 of  $K$ ,
- 117 • Grinding/crushing of material, to increase the interaction surface,
- 118 • Heating, because higher temperature normally increases the dissolution ability  
119 of solute in the solvent.

120 Once this external intensification is performed, internal diffusion becomes the limiting  
121 phenomenon. Most of solvent extraction operations are then regimented by the complex  
122 phenomena of solvent penetration in the solid, dissolution of solute in the solvent, and  
123 diffusion of solute in the internal solvent within the solid matrix. Thus, the driving force of  
124 these transfer phenomena can be assumed as a gradient of density ratio (Allaf, Besombes et  
125 al. 2011).

$$\frac{\rho_e}{\rho_{matrix}} (\vec{v}_e - \vec{v}_{matrix}) = -D_{eff} \vec{\nabla} \left( \frac{\rho_e}{\rho_{matrix}} \right) \quad Eq. 3$$

126 Where:

127  $(\vec{v}_e - \vec{v}_{matrix})$  is the relative velocity of the solute ( $m s^{-1}$ ) to solid dry material, ( $m s^{-1}$ ).

128  $\rho_e$  is the apparent density of the solute within the porous solid, ( $kg m^{-3}$ ).

129 Because of the absence of expansion, shrinkage...,  $v_{matrix}=0$  and  $\rho_{matrix} = \text{constant}$ .

$$\rho_e \vec{v}_e = -D_{eff} \vec{\nabla} \rho_e \quad Eq. 4$$

130 Through this formulation of both Eq. 2 and Eq. 4, the washing/diffusion model  
131 developed by (Allaf, Zougali et al. 2014) has the advantage to simplify the insertion of the  
132 solute movement within the solvent in the porous solid matrix. Extraction process kinetics  
133 should be analyzed through two stages of:

- 134 1. "washing"; disclosed by the starting accessibility  $\delta Y_s$  (expressed in kg of extract  
135 per kg of dry material): it is the amount of extract removed in very short time (t

136 near 0) from the interaction surface. The interaction between the solvent and  
 137 the exchanging surface takes place over this short time frame. The external  
 138 solvent dissolves the superficial solute. The intensification of this stage should  
 139 imply a dynamic convection (Amor, Lamy et al. 2008, Ben Amor and Allaf 2009)  
 140 instead of external diffusion.

141 2. and an internal diffusion. Since the “washing” stage removes some part of  
 142 solute from the sample surface, a solute gradient takes place between the core  
 143 and surface of the matrix. This acts as a driving force of the internal effective  
 144 diffusion of solute in the solvent within the porous matrix solids (Allaf 2009).  
 145  $D_{eff}$  ( $m^2 s^{-1}$ ) acts as the effective diffusivity of a similar Fick’s law (Allaf,  
 146 Besombes et al. 2011).

147 The whole extraction process involved in the first stage (solvent interacting with the  
 148 exchange surface) do not have to be involved in the diffusion model part.

149 By adding continuity to Fick’s-type law (Allaf, Besombes et al. 2011) and by assuming  
 150 the homogeneity of both temperature and structure within the matrix, (Mounir and Allaf  
 151 2008) proposed effective diffusivity  $D_{eff}$  constant; Eq. 4 becomes:

$$\frac{\partial \rho_e}{\partial t} = -D_{eff} \frac{\partial^2 \rho_e}{\partial r^2} \quad Eq. 5$$

152 Where  $r$  is the spherical coordinate. We opted to reveal the main solutions required  
 153 for this diffusion model from the standard Crank’s solutions. It is worth noting that the  
 154 experimental data to be considered are that involving the only effective diffusion ( $t > t_0$ ).

$$\frac{(Y_{\infty} - Y)}{(Y_{\infty} - Y_{t=t_0})} = \sum_{i=1}^{\infty} \frac{6}{i^2 \pi^2} \exp\left(-\frac{i^2 \pi^2}{d_p^2} D_{eff} (t - t_0)\right) \quad Eq. 6$$

155 By limiting this series to its first-term approach, Crank’s solution for the spherical form  
 156 of solid becomes:

$$\frac{(Y_{\infty} - Y)}{(Y_{\infty} - Y_{t=t_0})} = \exp(-k(t - t_0)) \quad Eq. 7$$

$$\ln\left(\frac{(Y_{\infty} - Y)}{(Y_{\infty} - Y_{t=t_0})}\right) = -k(t - t_0) \quad \text{Eq. 8}$$

157  $Y$ : The quantity of extracted solute (oil) at time  $t$  (kg/kg ddb),

158  $Y_{\infty}$ : The maximal quantity of extracted solute (oil)  $Y$  when  $t \rightarrow \infty$ ,

159  $Y_{t=t_0}$ : The quantity of solute (oil) at the beginning of the stage only concerned by  
160 the internal diffusion stage.

161 The correspondence between experimental data and model-diffusion is performed to  
162 calculate the effective diffusivity  $D_{eff}$  using Crank polynomial expression:

$$D_{eff} = \frac{d^2}{\pi^2} k \quad \text{Eq. 9}$$

163 Extrapolation of this diffusion model until  $t=0$  min can be used to determine the  
164 theoretical diffusion value  $Y_0$ . The difference between this calculated value  $Y_0$  and the initial  
165 experimental value  $Y_i=0$  corresponds to the starting accessibility on a dry dry basis ddb  
166 (matrix from which water and solute (oil) are removed):

$$\delta Y_s = Y_0 - Y_i = Y_0 \quad \text{Eq. 10}$$

## 167 **2 Materials and methods**

### 168 **2.1 RM and Chemicals**

169 Date seeds were acquired from the National Institute of Arid Zone (Degach, Tunisia).  
170 Initial water content  $W_i$  was measured  $8\% \pm 0.2$  dry basis (db). Dried seeds were isolated from  
171 full ripeness date fruit "Tamer stage".

172 n-Hexane was the only solvent we used for oil extraction. It was purchased from Carlo  
173 Erba (Val de Reuil, France) with 99.99% purity.

### 174 **2.2 Treatment operations**

175 The protocol of the treatment operations including assessments is illustrated in Figure  
176 1.

177

178

*Figure 1. Protocol for the extraction of oil from Tunisian date seeds*

179 **2.2.1 *Sorting and cleaning***

180 Date seeds were separated from the fruit manually. They were washed with distilled  
181 water to free them of any adhering date flesh and then dried (12 h) at about 40 °C. After  
182 drying, the seeds were stored in sealed polythene bags.

183 **2.2.2 *Grinding and Sieving***

184 10 kg of date seeds were ground in a heavy-duty grinder (National Institute of Arid  
185 Zone Degach, Tunisia) for 3 min. After grinding, the particle sizes of powders were measured  
186 by screening with a sieve machine (FRITSCH, Germany), with 1.5 mm as amplitude for 10 min  
187 of sieving time. Particle sizes were ranged from 0.2 to 1.4 mm. An appropriate quantity of  
188 powdered date seeds was kept at 4 °C.

189 **2.2.3 *Instant controlled pressure drop***

190 ***Equipment and laboratory scale unit***

191 The experimental DIC setup is composed of three main elements: (1) A high-  
192 temperature; high-pressure treatment vessel; with a suitable heating gas ;(2) A vacuum  
193 system with a vacuum tank with a volume 100 times greater than the processing vessel, and  
194 an adequate vacuum pump for maintaining an initial vacuum level of about 5 kPa in all the  
195 experiments and (3) An instant opening pneumatic valve between the vacuum tank and the  
196 processing vessel; it can be opened in less than 0.2 s; this ensures the abrupt pressure drop  
197 within the treatment vessel.

198 A data acquisition and automation system takes into account of numerous pressure,  
199 temperature, and time parameters. It is connected to a personal computer, establishing  
200 combination with the manual control of the system.

201 ***Treatment operating parameters***

202 Dried powder of date seeds (50 g) at  $8\pm 0.2\%$  db (dry basis), was firstly placed in the DIC  
203 treatment vessel (between 20 and 70 s). A first vacuum stage was established in order to  
204 reduce the resistance between the exchange surface and the saturated steam, which acts

205 instantaneously (in less than 1 s) as a heating fluid by condensation. Heat transfer inside the  
206 raw material is performed by effective conduction, strictly correlated with condensed water  
207 diffusion.

208 An abrupt pressure drop towards a vacuum systematically follows the thermal  
209 treatment. It results in an instant autovaporisation inducing an “instant” cooling of the solid  
210 material. After their DIC texturing, date seeds were recovered and ready for extraction  
211 (Figure 2).

212

213 *Figure 2. Temperature and pressure history of a DIC processing cycle.*

### 214 ***Experimental design***

215 We first carried out some preliminary experiments to identify the global impact of the  
216 texturing treatment, the most important operative parameters, and their ranges. The main  
217 operative parameters were the steam pressure P and the thermal treatment time t. P was  
218 ranged between 0.1 and 0.7 MPa and t from 20 to 70 s. This time should assure the  
219 homogeneity of both temperature and water content inside the particle. Optimization of DIC  
220 operating parameters was performed using Response Surface Methodology (RSM) with a 2-  
221 parameter; 5-level central composite experimental design. Thus we could reduce the  
222 experimental trials to 13 implying  $2^k=4$  factorial points;  $2k=4$  star points with five repetitions  
223 for the central point; k is the number of operating parameters used in the experimental  
224 design (Table 1).

225 The experiments were run in random in order to minimize the effects of unexpected  
226 errors due to extraneous factors.

227 *Table 1 Independent variable and levels used in treatment experimental process*

228 Since we used an orthogonal factorial design,  $\alpha$  is the axial distance

$$\alpha = \sqrt[4]{n} = \sqrt[4]{2^k} \quad \text{Eq. 11}$$

229 In the present case,  $k=2$ , the number of factorial trials is  $n=4$  and  $\alpha = 1.414213562$ .

230 Various extraction process parameters such as yields and kinetic model parameters,  
231 were assessed and considered as the responses (dependent variables). Their values were

232 introduced in the analysis design procedure of Statgraphics Software (MANUGISTICS Inc.,  
233 Rockville, USA). It enables the interpretation of the results, optimization of the treatment by  
234 multidimensional ways through recognizing the measured response variables Y by fitted  
235 second order polynomial models versus operating parameters  $X_i$  as factors:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \varepsilon \quad \text{Eq. 12}$$

236 Where  $\beta_{ii}$ ,  $\beta_{ij}$ ,  $\beta_i$ : are regression coefficients,  $\varepsilon$ : is the random error, and  $i$  and  $j$ : are  
237 the indices of factors.

238 RSM empirical polynomial model is used to optimize the factors. Experimental results  
239 allow determining the ANALyses Of VARIance (ANOVA), which are performed to determine  
240 significant differences between independent variables. Thus, the adequacy and the  
241 significance of the model are analyzed by estimating the lack of correspondence, Fisher test  
242 value (F-value) and  $R^2$  from the evaluation of ANOVA. The independent variables have a  
243 statistical significance here proved at 5% probability level ( $p < 0.05$ ) and revealed through  
244 Pareto chart. Then to build response surface, the software uses the quadratic model  
245 equation.

#### 246 **2.2.4 Solvent extraction**

247 The study of the impact of particle size as well as texturing by DIC on oil extraction was  
248 performed by determining the yields using Accelerated Solvent Extraction (ASE), and the  
249 kinetics through Dynamic Maceration (DM); both using n-hexane as solvent.

#### 250 **Dynamic Maceration (DM)**

251 The Dynamic Maceration DM was performed in an extraction batch with stirring. A  
252 quantity of 1.5 g of concerned powder was added to 15 ml of n-Hexane. A magnetic stirring  
253 at 400 rpm assured the homogeneity and intensification of the operation. The extraction  
254 was replicated many times, and different interval times were used to establish the kinetics.

255 Extracts were syringed and filtered at 0.2  $\mu\text{m}$  PTFE filters.. The obtained mixtures  
256 (hexane/oil solutions) were separated under vacuum by nitrogen flow.

257 ***Accelerated Solvent Extraction (ASE)***

258 Hexane ASE oil extraction was optimized by Kraujalis, Venskutonis et al. (2013). In the  
259 present work, ASE was a Dionex ASE 350 system (Thermo Fisher scientifique, Sunnyvale, CA,  
260 USA). The suitable ASE conditions were defined after preliminary tests. Samples of 7 g of  
261 date seed powder were mixed with 1 or 2 g of diatomaceous earth and placed in a 34 ml/2.9  
262 cm diameter stainless-cell. Typically, solvent presented 60% of the cell volume.

263 ASE treatment normally started by a 5 min heating time to let cell temperature reach  
264 100 °C at 10 MPa. These conditions allow hexane to remain in liquid phase. ASE process was  
265 performed for 4 cycles of 10 min each.

266 Then, cell content was purged by nitrogen for 150 s to remove impurities and collect  
267 the extract in the vial. After removing solvent in a rotary vacuum evaporator at 40 °C,  
268 obtained seed oils were drained under a stream of nitrogen and weighted afterwards by  
269 analytical balances and finally stored in a freezer (-4 °C) for subsequent chemical analyses.  
270 The oil yields were calculated in g oil/g ddb ±0.05 g/g ddb (dry-dry basis); ddb concerns  
271 material which excludes both water and oil contents.

$$Y = \%extract(ddb) = \frac{\text{weight of extract obtained after extraction}}{\text{weight of dry dry basis of seeds (ddb)}} \quad \text{Eq. 13}$$

272 **2.3 Assessments and characterization**

273 **2.3.1 Measure of moisture content**

274 The moisture content of the samples was determined according to AFNOR (NF V03-  
275 708) method. A quantity of 5 g of powder was heated at 105 °C for 24 h in an adequate  
276 airflow oven (AIR CONCEPT-Fir LABO, AC 60).

277 The moisture content was expressed as percentage dry basis db ± 0.2% db.

278 A “Sartorius” infrared moisture analyzer was also used (Matter Toledo LP-16 Infrared  
279 Dryer/Moisture Analyzer (Bishop International Akron, OH – USA). The results obtained were  
280 fairly consistent with those of the oven.

### 281 **2.3.2 Oil composition**

282 A quantity of 40 mg oil was converted to methyl esters by adding 1 ml of n-hexane  
283 followed by 200  $\mu\text{L}$  of sodium methoxide (2M). The mixture was maintained at 50  $^{\circ}\text{C}$  for 1h  
284 then added to 200  $\mu\text{L}$  of HCL (2M). Then, 0.5 ml of distilled water was added. Therefore, the  
285 extracted fatty acid methyl esters (FAME<sub>s</sub>) were dissolved in pure hexane and 1  $\mu\text{L}$  was  
286 injected into GC-MS.

287 GC-MS analyses were performed using Agilent 19091S-433 GC (Gas Chromatography).  
288 The instrument was equipped with a HP-5MS (5% Phenyl Methyl Siloxane) capillary column  
289 (30 m x 350  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ). The average of velocity of the carrier gas (He) was at 37  $\text{cm s}^{-1}$ .  
290 Injection of 1  $\mu\text{L}$  of the various samples was carried out with a split mode (ratio 1:20) and the  
291 injector temperature was set at 270  $^{\circ}\text{C}$ . The oven temperature increased from 70 to 200  $^{\circ}\text{C}$   
292 at a rate of 5  $^{\circ}\text{C}/\text{min}$ , and from 200 to 260  $^{\circ}\text{C}$  at a rate of 2  $^{\circ}\text{C}/\text{min}$ , to be held at 325  $^{\circ}\text{C}$  for 50  
293 min. The mass spectra were recorded at 3 scans/s between 50 to 400 amu. The ionization  
294 mode was electron impact (EI) at 70 eV. Identification of common fatty acids was performed  
295 using the NIST'98 [US National Institute of Standards and Technology (NIST), Gaithersburg,  
296 MD, USA] mass spectral database.

### 297 **2.4 The main Responses for identification extraction operation**

298 The quantification of the intensification effects was performed through yields  $Y_{\infty}$  (g/g  
299 ddb) and kinetics extraction, which were the starting accessibility  $\delta Y_s$  (g/g ddb), the effective  
300 diffusivity  $D_{eff}$  ( $\text{m}^2 \text{s}^{-1}$ ), and the Relative Extraction Time RET based on untextured material  
301 (%). Yields were issued from ASE measurements, while kinetic parameters were gathered  
302 from the DM data through the phenomenological model of surface-interaction (washing) /  
303 internal diffusion.

304 Optimization of solvent extraction process aimed at getting the highest values of  $Y_{\infty}$ ,  
305  $\delta Y_s$ , and  $D_{eff}$ , and the lowest value of RET.

306 In our study of process modeling, we used at first ASE experimental data to determine  
307 the final oil yield  $Y_{\infty}$  in the relative diffusion extraction:

$$\frac{Y - Y_{t_0}}{Y_{\infty} - Y_{t_0}} = f(t) \quad \text{Eq. 14}$$

308 Experimental data concerning this diffusion stage were gotten for time  $t > t_0$  for which  
309 we assumed that diffusion was the limiting factor. It is worth noting that these concerned  
310 experimental data implied in diffusion model must exclude those close to the initial time.  
311 The last part of the kinetic curve was also ejected once their evolution versus time is lower  
312 than measurement incertitude points or possibly implying solute degradation.

313 The difference between the value  $Y_o$  calculated by extrapolating the diffusion model  
314 until the initial time  $t=0$  and the experimental value  $Y_i=0$  corresponds to the starting  
315 accessibility  $\delta Y_s$  on dry dry basis (Figure 3):

$$\delta Y_s = Y_o - Y_i = Y_o - 0 \quad \text{Eq. 15}$$

316

317 *Figure 3. Determination of the effective diffusivity  $D_{eff}$  and the starting accessibility  $\delta Y_s$  from*  
318 *experimental data of DM extraction kinetics and diffusion model.*

## 319 **3 Results and Discussions**

### 320 **3.1 Oil extraction from coarsely ground date seeds**

#### 321 **3.1.1 Global Approach**

322 The results of oil extraction from coarsely ground date seed powder were summarized  
323 in Table 2. Applied on raw material, ASE yields were higher than those obtained in 8 h DM  
324 (dynamic maceration). They were  $11.35 \pm 0.1\%$  and  $9.1 \pm 0.04\%$  ddb, respectively.

325 The impacts of DIC texturing conditions were first studied based on ASE oil extraction  
326 yields. As expected, yields of ASE extracted oil from coarsely grounded date seeds were  
327 higher from differently DIC treated seed powders than untreated raw material, with  
328  $14.15 \pm 0.08\%$  and  $11.35 \pm 0.02\%$  ddb, respectively. Furthermore, similar effects were obtained  
329 with 2 h DM oil extraction. Yields were  $11.28 \pm 0.10\%$  against  $7.47 \pm 0.04\%$  ddb for DIC  
330 textured and untreated powders, respectively. Hence, adequate texturing by DIC  
331 dramatically increases the availability of plant-based compounds (Ben Amor and Allaf 2009,  
332 Allaf 2013). The potentiality of using DIC treatment as intensifying way of oil extraction can  
333 be more appreciated by introducing **RTO Ratio of Total Oil extraction**. RTO is defined as the

334 **ratio of yields** after 2 h of DM oil extraction reported to the maximum oil extracted from raw  
335 material with ASE.

$$RTO = \frac{Y_{DM;2h}}{Y_{ASE;RM}} \quad \text{Eq. 16}$$

336 However, to better highlight the comparative impact of DIC texturing, we defined a  
337 "Ratio of Improvement in total oil Extraction RIE" as the relative increasing of 2-h DM oil  
338 extraction from DIC samples reported to the untreated material (RM):

$$RIE = \frac{Y_{DM;DIC;2h} - Y_{DM;RM;2h}}{Y_{DM;RM;2h}} \quad \text{Eq. 17}$$

339 RTO and RIE reached values up to 101% and 26%, respectively

340 *Table 2 Results of date seed oil yields after Accelerated Solvent Extraction ASE and Dynamic*  
341 *Maceration DM extraction Statistics and Design of Experiments DoE*

342 Analysis of variance (ANOVA) was carried out and revealed by Pareto chart on the data  
343 using STATGRAPHICS to identify the effect significance of different experimental factors on  
344 the dependent variables of  $Y_{\infty}$ ,  $\delta Y_S$ ,  $D_{eff}$ , RTO, and RIE. In Table 2, oil yields are given versus  
345 various DIC parameters, for both ASE (at 100°C, 1 MPa and for 40 min as time extraction)  
346 and DM (at ambient temperature and for 2 h extraction time) methods.

#### 347 ***Effect of DIC parameters on ASE oil extraction yields***

348 Let's firstly note that DIC saturated steam pressure in the treatment vessel reveals the  
349 thermal level of treatment. The optimization of DIC treatment conditions was based on ASE  
350 yields  $Y_{ASE}$  as the main response parameter (Table 2). Pareto chart, General Trends,  
351 Response Surface and Iso-Response for  $Y_{ASE}$  oil yields from date seed powder were  
352 determined in Figure 4 (A, B, C, D). In Pareto chart histogram, the effect is considered as  
353 statistically significant if the corresponding factor crosses the vertical 5% significance line.

354

355 *Figure 4. Effect of DIC parameters on the total ASE oil extraction yields of date seed powder: A)*  
356 *Standardized Pareto Chart; B) Main Effects Plot; C) Estimated Response Surface, and D) Iso-Response.*

357 In these statistical limits, and the ranges of operating parameters, the linear steam  
358 pressure P value was the most significant effect followed by linear effect of the treatment  
359 time t. The favor effect of P and t on the operation is illustrated by their positive values.  
360 Thus, in the considered ranges, the higher the values of P and t, the higher the ASE extracted  
361 oil. The second-order empirical regression model of ASE yields versus DIC parameters had a  
362 regression coefficient  $R^2=0.88$ , which means a good fit with experiments.

$$Y_{ASE} = 13.59 + 0.62P + 0.012t + 0.20P^2 - 0.009Pt - 0.00006t^2 \quad \text{Eq. 18}$$

363 Where:  $Y_{ASE}$  is expressed in % ddb; P in MPa; and t in s.

364 From Eq. 18 regression model, it was possible to optimize DIC operating conditions and the  
365 highest value of the oil yields of  $Y_{ASE}= 14.29\%$  ddb was achieved at P = 0.8 MPa and t = 38 s.

### 366 ***Effect of DIC parameters on Dynamic Maceration (DM) extraction kinetics***

#### 367 **General results**

368 Experimental results obtained from Dynamic Maceration (DM) extraction of oil from  
369 date seeds are presented in Figure 5. As expected, DIC texturing pretreatment implied  
370 increasing of oil quantity in comparison with untreated particles.

371 The yield obtained after 2 h extraction reaches a maximum value of 11.28 to  
372  $11.42\pm 0.08\%$  ddb for DIC treatments against  $7.5\pm 0.05\%$  ddb for controlled raw material. Oil  
373 yield of raw material could increase versus time and the maximum value of 8% ddb was  
374 obtained after 8 h while a value of 11% was reached after 24 h of extraction. Whereas, the  
375 oil yield obtained in 8 h of extraction of DIC textured seeds was 12 % ddb. It was clear that  
376 whatever DIC treatments, we could obtain in 30 min the same oil yield as that occurred by  
377 raw material after 8 h of dynamic maceration DM. We can deduce the efficiency of DIC  
378 treatment in intensifying extraction kinetics from date seed powder.

379

380 *Figure 5. Kinetics of oil extraction from various DIC textured date seeds powder*

381 Starting accessibility and Effective diffusivity

382 Table 2 showed that the effective diffusivity  $D_{\text{eff}}$  of the treated DIC textured samples  
383 reached values of 8.9 to 10.1  $10^{-12} \text{ m}^2 \text{ s}^{-1}$ , while it was about 8.7  $10^{-12} \text{ m}^2 \text{ s}^{-1}$  for untreated  
384 sample (RM), which means a great increasing of kinetics.

385 DIC texturing treatment significantly improved the starting accessibility  $\delta Y_s$  by more  
386 than 71% to be up to 10.13% instead of 6.14% ddb for untreated seeds.

387 Figure 6 shows the significant effect of DIC saturated steam pressure and thermal  
388 treatment time. General trends and Response surface were also relevant to illustrate the  
389 significant effect of the operating parameters. The second-order empirical regression model  
390 of starting accessibility versus DIC parameters was established with a regression coefficient  
391  $R^2$  equal to 0.78%, which is an acceptable fit with experiments.

$$\delta Y_s = 8.67 + 1.918P + 0.0228t - 1.35204P^2 - 0.00198Pt - 0.000016t^2 \quad \text{Eq. 19}$$

392  
393 *Figure 6. Effect of DIC parameters on starting accessibility: Standardized Pareto Chart A; Main Effects*  
394 *Plot B; Estimated Response Surface C, and Iso-Response D*

395 The impact of DIC texturing as a specific pretreatment prior to solvent extraction was  
396 very important compared to untreated raw material. Thus,  $D_{\text{eff}}$  values were 10.12  $10^{-12}$   
397 against 8.7  $10^{-12} \text{ m}^2 \text{ s}^{-1}$  for DIC treated and untreated raw material, respectively. However,  
398 Pareto chart histograms for effective diffusivity  $D_{\text{eff}}$  show slowest effect of DIC parameters.  
399 This means that the range of operative parameters was too focused.

400 Oil extraction yields

401 RSM study was performed with various kinetic parameters versus DIC operating  
402 parameters P and t. Pareto Chart obtained from experimental data of DM oil extraction  
403 yields in Figure 7, showed the significant effect of saturated steam pressure P and the  
404 treatment time t through its interaction with P. Whereas, t did not have a major influence.  
405 General trends and Response surface were also relevant to illustrate these significant  
406 effects. Here too, the second-order empirical regression model of DM yields versus DIC  
407 parameters had a regression coefficient  $R^2=0.94\%$ , revealing a proper fitting to experiments.

$$Y_{DM;\infty} = 12.27 + 1.3P - 0.0005t - 1.17914P^2 + 0.01Pt - 0.00004t^2 \quad \text{Eq. 20}$$

408 Where:  $Y_{DM;\infty}$  is expressed in % ddb; P in MPa; and t in s.

409 The same optimized DIC parameters  $P = 0.8$  MPa and  $t = 70$  s were obtained with a  
410 maximum oil yields of DM  $Y_{DM;\infty} = 13.01\%$  ddb.

411

412 *Figure 7. Effect of DIC parameters on total DM oil extraction yield: A) Standardized Pareto Chart; B)*  
413 *Main Effects Plot; C) Estimated Response Surface, and D) Iso-Responses.*

## 414 **3.2 Impact of particle size on oil yields and kinetics**

415 The second part of this study concerned the impact of grinding and particle size on the  
416 ability of the oil extraction. ASE and DM were used with different particle sizes (0.2 to 1.4  
417 mm) of powder from raw material and DIC textured samples. Measurements of ASE oil yields  
418  $Y_{ASE}$  and DM Oil yields versus time were carried out and compared.

### 419 **3.2.1 Oil Yields**

420 Final yields ( $Y_{ASE}$ ) in Table 3 showed that whatever the particle size, DIC treatments  
421 allowed final oil extraction yields to be always 30-50% higher than those obtained with  
422 untreated samples.

423 With 8 h DM extraction, oil yield reached  $10.49 \pm 0.05\%$  ddb for the smallest particle  
424 size while it was only 4.57% for biggest particle size. Even after 2 h DM extraction, it was  
425 possible to obtain the same or more oil yield from the smallest particle size powder than in 8  
426 h from the biggest particle size powder. Indeed, DIC treated products allowed extracting in  
427 two hours 11.62% ddb, which was higher than the amount usually obtained after 8 h with  
428 the non DIC pretreated raw material (10.49% ddb).

429 *Table 3. Oil yields from different particle size of date seeds.*

430 Furthermore, in all cases of DIC textured powders, it was possible to obtain after 30  
431 min of DM extraction, the same amount of oil that was obtained by DM extraction of 2 h  
432 from the untreated product. To better highlight the comparative aspect of our study, we  
433 compared the relative availability of oil extraction from DIC samples with the untreated  
434 material (RM) using the "Ratio of Improvement in total oil Extraction RIE" as one of the main

435 response parameters (Eq. 17). RIE average value of the RSM samples was about  $27.4 \pm 0.05\%$ ,  
436 varying from 16% to 35% depending on particle size.

437 The Ratio of Total Oil extraction RTO (Eq. 16) was also used to deduce that, separately  
438 in the both situations of untreated and DIC treated powders, the smaller the particle size,  
439 the higher the oil yield.

### 440 **3.2.2 Kinetics of total extraction**

441 All experimental results obtained from extraction kinetics of DIC treated date seed  
442 powders (Figure 8), show that decreasing sample size implied increasing of oil quantity,  
443 which systematically were higher than untreated considered powders.

444 Thus, 2 h DM extraction allowed obtaining oil yields of 3.47% ddb for 1.4 mm particle.  
445 This amount was increasing with decreasing particle size to become 9.54% ddb for the  
446 smallest untreated seeds (0.2 mm). The same behavior was observed with DIC treated seed  
447 powders. And when DM extraction was performed for the same time, this value increased  
448 from 4.67% to 11.62% ddb, respectively. The highest improvement issued from DIC  
449 treatment was revealed by  $RIE = 34.58 \pm 0.05\%$  for powders of 1.4 mm particle size.

450 Obviously, oil yield was remarkably as higher as the particle size was smaller and much  
451 more when powders were DIC textured. This can be attributed to the fact that the smaller  
452 the particle size, the larger the specific surface area and the shorter the mass transfer  
453 distance. The oil is being isolated much more efficiently by reducing the particle size of  
454 powder. Furthermore, DIC texturing generates reduction of treatment time, increases yields  
455 and improves extraction kinetics. Higher extraction availability thus triggered should be due  
456 to its possible disruption of cell walls where oil is located in date seeds. So, larger contact  
457 area between solvent and material was created and more oil extraction was appeared at the  
458 surface as starting accessibility.

459

460 *Figure 8. Extraction kinetics of date seed oil*

461 The kinetic parameters of starting accessibility  $\delta Y_s$  (% ddb), effective diffusivity  $D_{eff}$   
462 ( $m^2 s^{-1}$ ), and DM yield  $Y_{t=2h}$  (% ddb) are summarized in Table 4 for different cases:

463 *Table 4. Starting accessibility  $\delta Y_s$ , effective diffusivity  $D_{eff}$ , and oil yield after 2 h DM extraction*  
464  *$Y_{t=2h}$  for 1.4 mm and 0.2 mm particle sizes.*

465 Experimental data should be utilized to identify the possible models revealing 1) the  
466 whole improvement resulted from DIC versus RM in terms of  $\delta Y_s$  and  $D_{eff}$ ; 2) the whole  
467 evolution of  $\delta Y_s$  versus the granule size D. Indeed, while  $D_{eff}$  should depend on various  
468 parameters such as D, availability of oil inside the residual cells, and permeability and  
469 tortuosity of the grain; a simplified empirical model of the starting accessibility versus D  
470 would exist to make global link with both surface and diameter D. Indeed, since it is evident  
471 that exchange area strictly depends on D, such model can get more the following form:

$$\delta Y_s = f(D) \quad \text{Eq. 21}$$

472 *Figure 9. Empirical models of relative evolution of extraction kinetics of DIC vs RM powders.*

473 The relative expression of DIC versus RM powders at corresponding granulometry for  
474 both  $D_{eff}$  and  $\delta Y_s$  offered about 15% improvement factor with  $R^2$  of 0.99 and 0.95,  
475 respectively (Figure 9; Figure 10), and (Eq. 22 and Eq. 23).

$$D_{eff}(\text{DIC}) = 1.1584D_{eff}(\text{RM}) + 1.301 \quad \text{Eq. 22}$$

with  $R^2 = 0.98904$

$$\delta Y_s(\text{DIC}) = 1.1517\delta Y_s(\text{RM}) - 0.0017 \quad \text{Eq. 23}$$

with  $R^2 = 0.9469$

476

477 *Figure 10. Empirical models of starting accessibility  $\delta Y_s$  versus the particle diameter of DIC and RM*  
478 *powders.*

479 These values of  $R^2$  translate the good relevance of these both empirical models. The  
480 global impact of DIC versus RM would be revealed by the fact that DM extraction time was  
481 264 min and 85 min for 1.4 and 0.2 mm diameter particle, respectively. While for DIC  
482 samples extraction time was 122.5 for 1.4 mm and 55 min for 0.2 mm particle diameter. The  
483 evolution of starting accessibility  $\delta Y_s$  vs particle diameter was calculated as linear correlation  
484 models for both RM and DIC-textured powders, respectively.

$$\delta Y_s(\text{RM}) = 9.96(1 - 171\pi D)\% \text{ ddb} \quad \text{Eq. 24}$$

with  $R^2 = 0.88274$

$$\delta Y_s(\text{DIC}) = 8.86(1 - 171\pi D)\% \text{ ddb} \quad \text{Eq. 25}$$

with  $R^2 = 0.9716$

485 Where  $D$  is expressed in  $m$  and  $\delta Y_s$  in % ddb.

486 Both RM and DIC textured powders presented similar behaviors in terms of starting  
487 accessibility evolution versus diameter.

488 Well-optimized DIC treatment coupled with the most realistic grinding operation  
489 should always present a very effective and relevant intensification way for the solvent oil  
490 extraction.

### 491 **3.3 Fatty acid composition**

492 The fatty acid methyl ester FAMES composition of the oils of the species is shown in  
493 Table 5. The most abundant fatty acids of date seed oil were oleic (C18:1), linoleic (C18:2),  
494 palmitic (C16:0), myristic (C14:0), and lauric (C12:0) which together composed about 90-95%  
495 of the total fatty acids.

496 The major fatty acids found in those cultivars for DIC treated and untreated samples  
497 were similar. They were oleic acid (47.81-53.14%, respectively), for Deglet Nour seed oil and  
498 from 44.88 % to 49.40% for Ftimi seed oil, followed by lauric acid (21.03-25.66%), myristic  
499 acid (10.28-11.66%), palmitic acid (9.11-10.53%), linoleic acid (7.05-7.80%), and Stearic acid  
500 (3.10-3.63%). Behenic acid (0.42-0.51%) and Arachidic acid (0.38-0.54%) were present in low  
501 amounts. These results are in general agreement with those done by (Besbes, Blecker et al.  
502 2004, Nehdi, Omri et al. 2010, Aris, Norhuda et al. 2013) (Aris, Norhuda et al. 2013). This  
503 similarity in fatty acid profiles of oils issued from RM untreated and DIC textured treated  
504 date seed powders should reflect the absence of any significant degradation triggered by DIC.  
505 Indeed, since DIC is a high-temperature short-time process with an abrupt pressure drop  
506 towards a vacuum resulting in instant cooling, optimized DIC treatment avoids any  
507 discernible thermal degradation.

508 *Table 5. Fatty acid profile (relative %) obtained via gas chromatography*

## 509 4 Conclusion

510 A great impact of texturing by DIC on the intensification of solvent extraction of date  
511 seed oil was observed. The results proved that DIC treatment had a positive impact on the  
512 oil extraction yields. Furthermore, regarding the extraction kinetics of different particle size  
513 of date seed powders; DIC treatment increased more than twice the starting accessibility  
514 while decreasing the effective diffusivity. Adequate Design of Experiments DoE allowed the  
515 optimization of DIC texturing parameters as saturated steam pressure  $P=0.8$  MPa and  
516 thermal treatment time  $t=70$  s. Then, it was possible to propose DIC as a pre-treatment  
517 texturing possibly coupled with grinding as technology-assisted solvent extraction process.  
518 These both modifications of the structure, when combined, greatly increase the  
519 technological abilities.

520 This enables a reduction in thermal treatment time, compared to traditional  
521 extraction, from 15 min to 20 s, with higher extraction yields and a consequent preservation  
522 of the product quality.

523 Further investigations about DIC treatment on both date seeds and flesh may reveal  
524 the presence of pharmacologically active compounds. Thus added other possibilities to have  
525 important income source for date growing macro economical impact of concerned  
526 countries.

## 527 Reference

- 528 Al-Hooti, S., J. Sidhu and H. Qabazard (1997). "Physicochemical characteristics of five date  
529 fruit cultivars grown in the United Arab Emirates." Plant Foods for Human Nutrition **50**(2):  
530 101-113.
- 531 Al-Qarawi, A., B. Ali, S. Al-Mougy and H. Mousa (2003). "Gastrointestinal transit in mice  
532 treated with various extracts of date (*Phoenix dactylifera* L.)." Food and chemical  
533 toxicology **41**(1): 37-39.
- 534 Allaf, K. (2009). The New instant controlled pressure – drop DIC technology. Essential Oils  
535 and Aromas: Green Extraction and Application. New Delhi, Chemat F.: 85-121.
- 536 Allaf, K., C. Besombes, B. Berka-Zougali, M. Kristiawan, V. Sobolik and T. Allaf (2011). Instant  
537 Controlled Pressure Drop Technology in Plant Extraction Processes. Enhancing Extraction  
538 Processes in the Food Industry. N. Lebovka, E. Vorobiev and F. Chemat. Dublin, Ireland, CRC  
539 Press Taylor & Francis Group: 255-302.
- 540 Allaf, T. (2013). Instant Controlled Pressure Drop for Green Extraction of Natural Products:  
541 Intensification & Combination. PhD, University of Avignon.

542 Allaf, T. and K. Allaf (2014). Instant Controlled Pressure Drop (D.I.C.) in Food Processing. New  
543 York, Springer.

544 Allaf, T., B. Zougali, C. Nguyen, M. Negm and K. Allaf (2014). DIC Texturing for Solvent  
545 Extraction. Instant Controlled Pressure Drop (D.I.C.) in Food Processing. T. Allaf and K. Allaf,  
546 Springer New York: 127-149.

547 Amor, B. B., C. Lamy, P. Andre and K. Allaf (2008). "Effect of instant controlled pressure drop  
548 treatments on the oligosaccharides extractability and microstructure of Tephrosia purpurea  
549 seeds." Journal of Chromatography A **1213**(2): 118-124.

550 Aris, N., I. Norhuda and I. Adeib (2013). "Extraction of Phoenix Dactylifera (Mariami) seeds oil  
551 using supercritical carbon dioxide (SC-CO<sub>2</sub>)." International Journal **4**(1).

552 Ben Amor, B. and K. Allaf (2009). "Impact of texturing using instant pressure drop treatment  
553 prior to solvent extraction of anthocyanins from Malaysian Roselle (*Hibiscus sabdariffa*)." Food Chemistry **115**(3): 820-825.

555 Besbes, S., C. Blecker, C. Deroanne, N.-E. Drira and H. Attia (2004). "Date seeds: chemical  
556 composition and characteristic profiles of the lipid fraction." Food Chemistry **84**(4): 577-584.

557 Besbes, S., C. Blecker, C. Deroanne, G. Lognay, N.-E. Drira and H. Attia (2005). "Heating  
558 effects on some quality characteristics of date seed oil." Food chemistry **91**(3): 469-476.

559 Besbes, S., C. Blecker, C. Deroanne, G. Lognay, N. Drira and H. Attia (2004). "Quality  
560 characteristics and oxidative stability of date seed oil during storage." Food science and  
561 technology international **10**(5): 333-338.

562 Borchani, C., S. Besbes, C. Blecker, M. Masmoudi, R. Baati and H. Attia (2010). "Chemical  
563 properties of 11 date cultivars and their corresponding fiber extracts." African Journal of  
564 Biotechnology **9**(26): 4096-4105.

565 Briones, R., L. Serrano, R. B. Younes, I. Mondragon and J. Labidi (2011). "Polyol production by  
566 chemical modification of date seeds." Industrial Crops and Products **34**(1): 1035-1040.

567 Chemat, F. and G. Cravotto (2013). Microwave-assisted Extraction for Bioactive Compounds.  
568 New York, Springer.

569 Desbois, A. P. (2012). "Potential applications of antimicrobial fatty acids in medicine,  
570 agriculture and other industries." Recent Pat Antiinfect Drug Discov **7**(2): 111-122.

571 Devshony, S., E. Eteshola and A. Shani (1992). "Characteristics and some potential  
572 applications of date palm (*Phoenix dactylifera* L.) seeds and seed oil." Journal of the  
573 American Oil Chemists Society **69**(6): 595-597.

574 FAO. (2010). "Statistical Databases." 2014, from <http://faostat.fao.org>.

575 Habib, H. M. and W. H. Ibrahim (2008). "Nutritional quality evaluation of eighteen date pit  
576 varieties." International journal of food sciences and nutrition **60**(S1): 99-111.

577 Hamada, J., I. Hashim and F. Sharif (2002). "Preliminary analysis and potential uses of date  
578 pits in foods." Food chemistry **76**(2): 135-137.

579 Kraujalis, P., P. R. Venskutonis, A. Pukalskas and R. Kazernavičiūtė (2013). "Accelerated  
580 solvent extraction of lipids from *Amaranthus* spp. seeds and characterization of their  
581 composition." LWT - Food Science and Technology **54**(2): 528-534.

582 Larrucea, E., A. Arellano, S. Santoyo and P. Ygartua (2001). "Combined effect of oleic acid  
583 and propylene glycol on the percutaneous penetration of tenoxicam and its retention in the  
584 skin." European Journal of Pharmaceutics and Biopharmaceutics **52**(2): 113-119.

585 Mounir, S. and K. Allaf (2008). "Three-Stage Spray Drying: New Process Involving Instant  
586 Controlled Pressure Drop." Drying Technology **26**(4): 452-463.

587 Munier, P. (1973). Le palmier dattier. Paris, Maisonnaive et Larose.

588 Nehdi, I., S. Omri, M. Khalil and S. Al-Resayes (2010). "Characteristics and chemical  
589 composition of date palm (< i> Phoenix canariensis</i>) seeds and seed oil." Industrial Crops  
590 and Products **32**(3): 360-365.

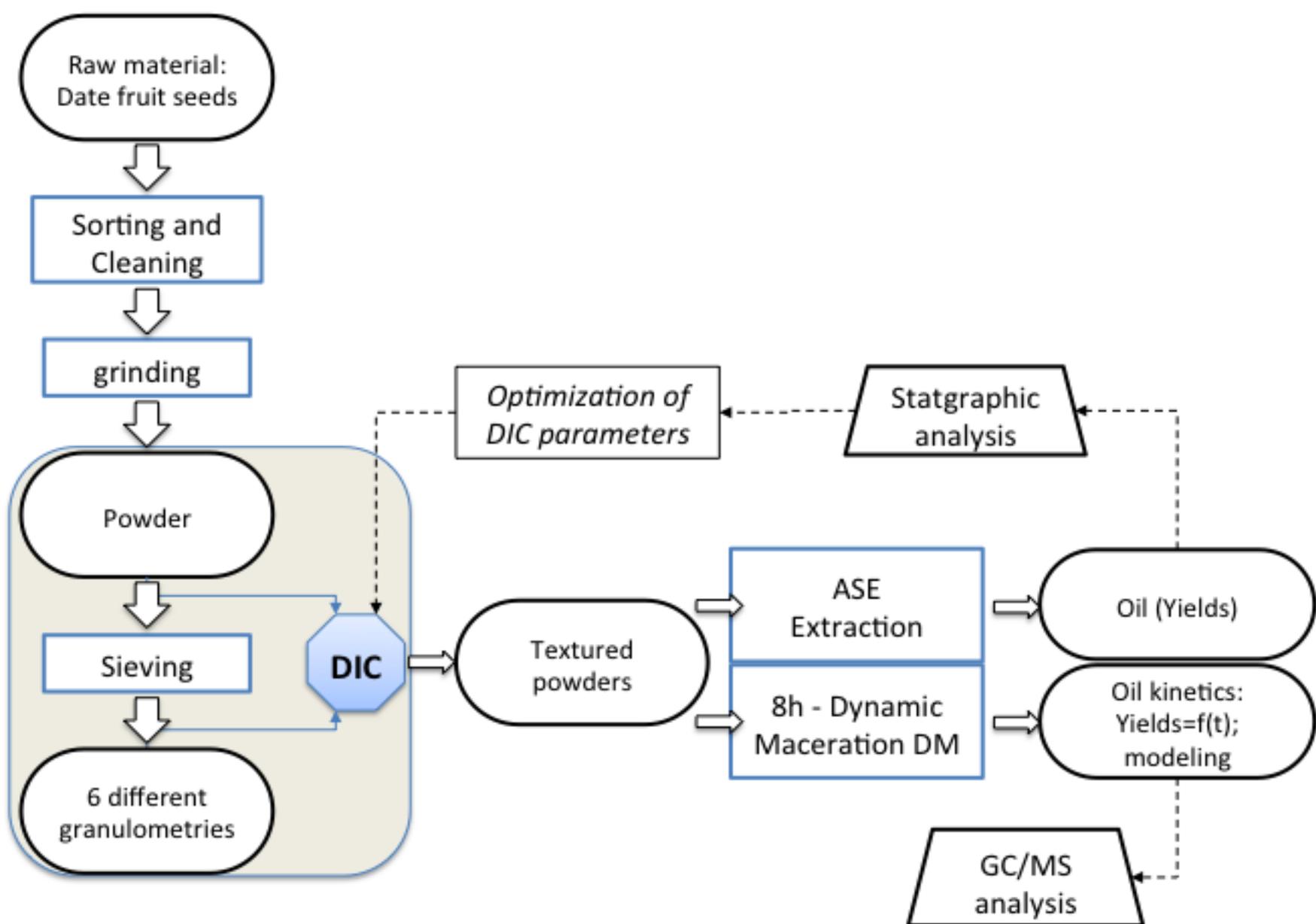
591 Pan, Z., W. Qu, H. Ma, G. G. Atungulu and T. H. McHugh (2011). "Continuous and pulsed  
592 ultrasound-assisted extractions of antioxidants from pomegranate peel." Ultrasonics  
593 Sonochemistry **18**(5): 1249-1257.

594 Rahman, M., S. Kasapis, N. Al-Kharusi, I. Al-Marhubi and A. Khan (2007). "Composition  
595 characterisation and thermal transition of date pits powders." Journal of food engineering  
596 **80**(1): 1-10.

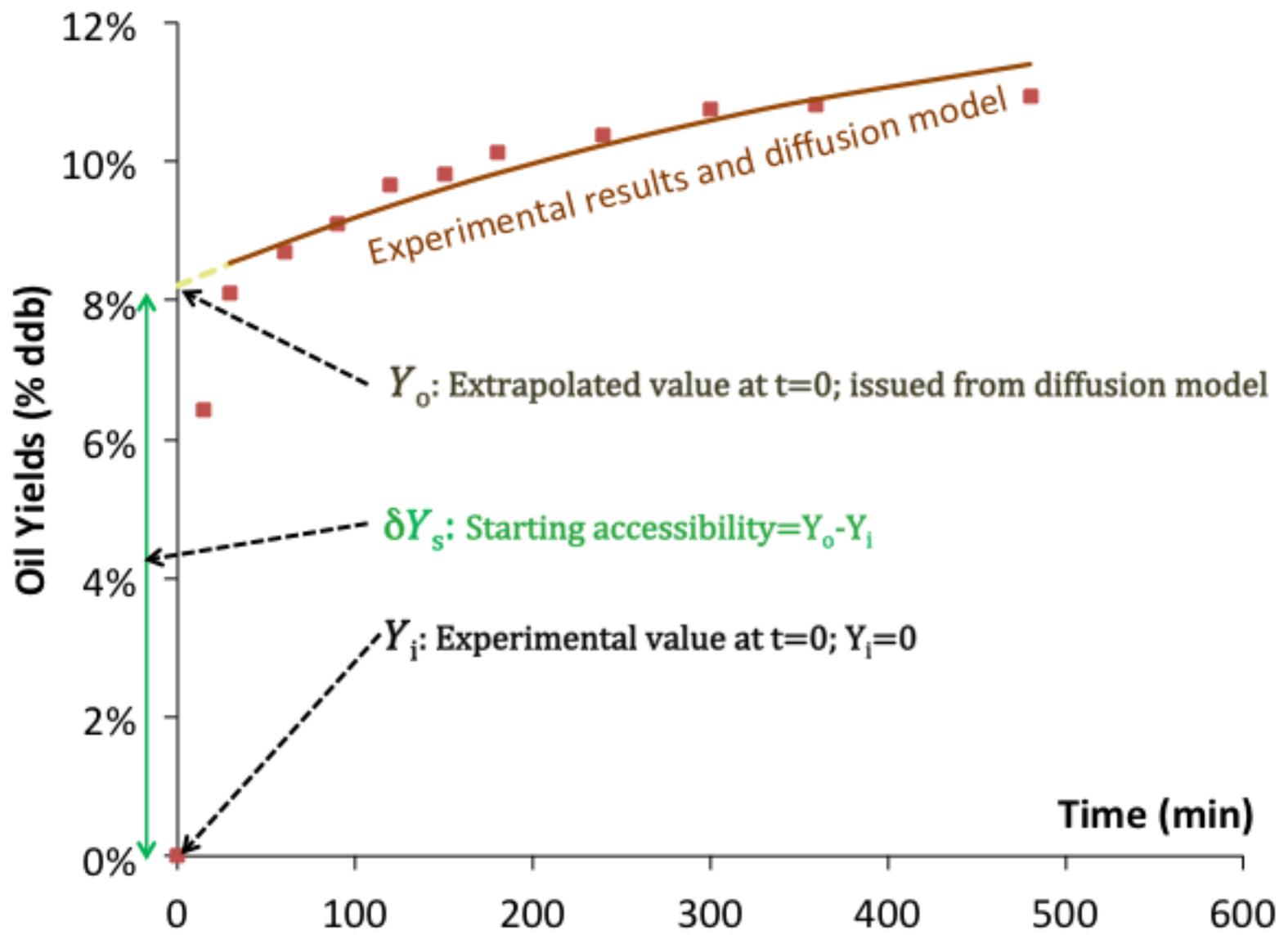
597 Rhouma, A. (1993). Le palmier dattier en Tunisie : Un secteur en pleine expansion. Le  
598 palmier dattier dans l'agriculture d'oasis des pays méditerranéens. M. Ferry and D. Greiner,  
599 Zaragoza : CIHEAM. **28**: 85-104.

600

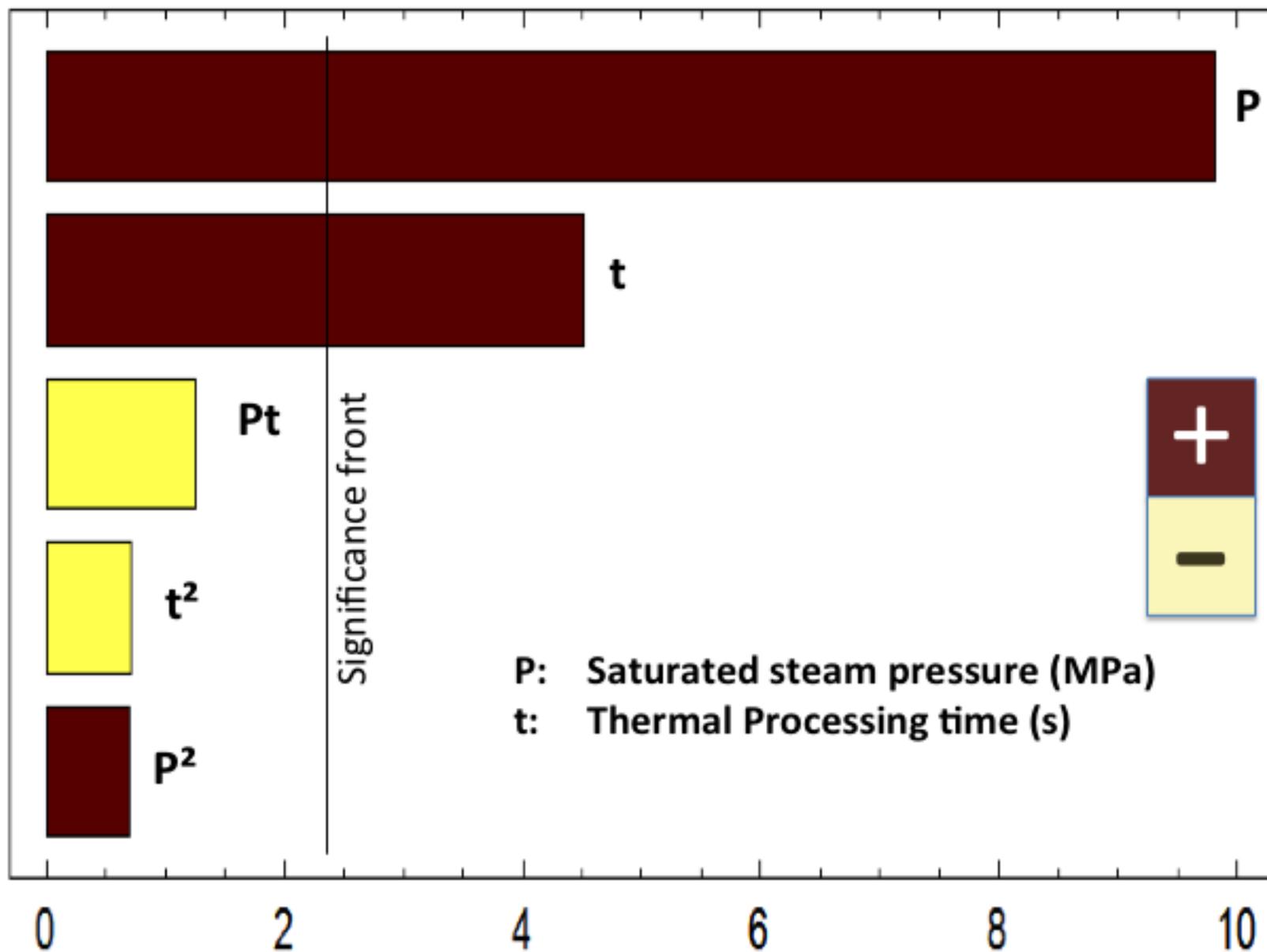
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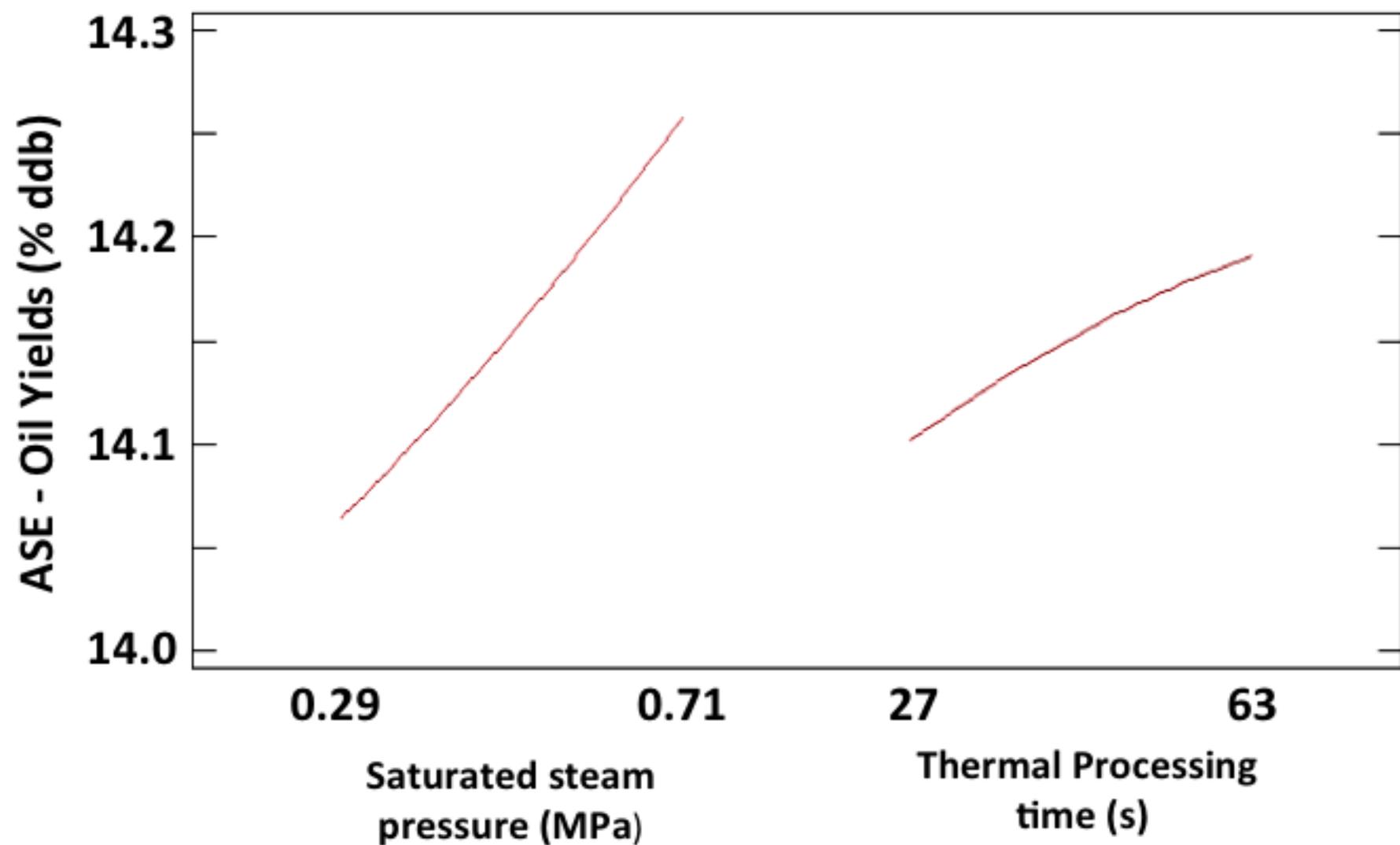




Standardized Pareto Chart for ASE Oil Yield (%ddb)

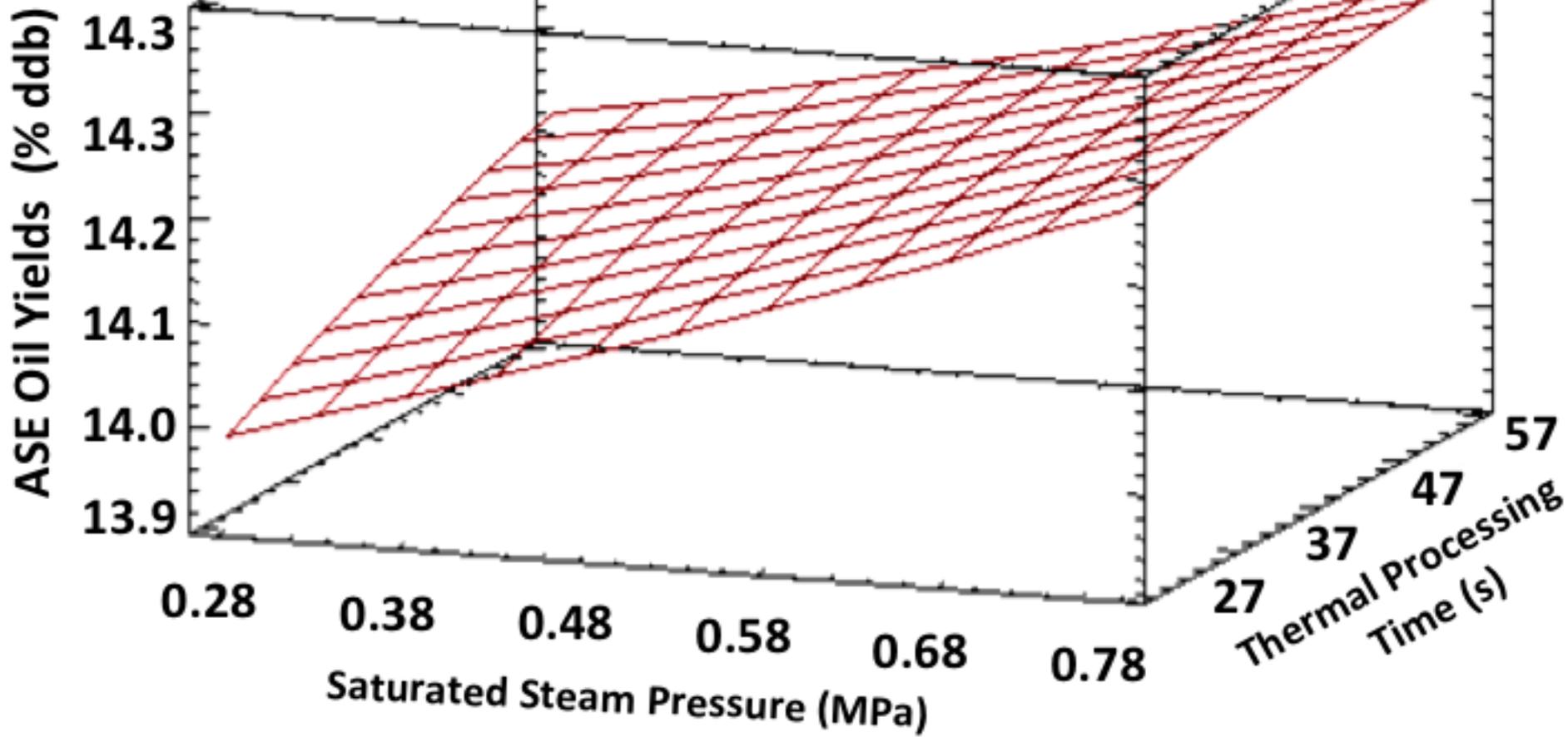


(B)



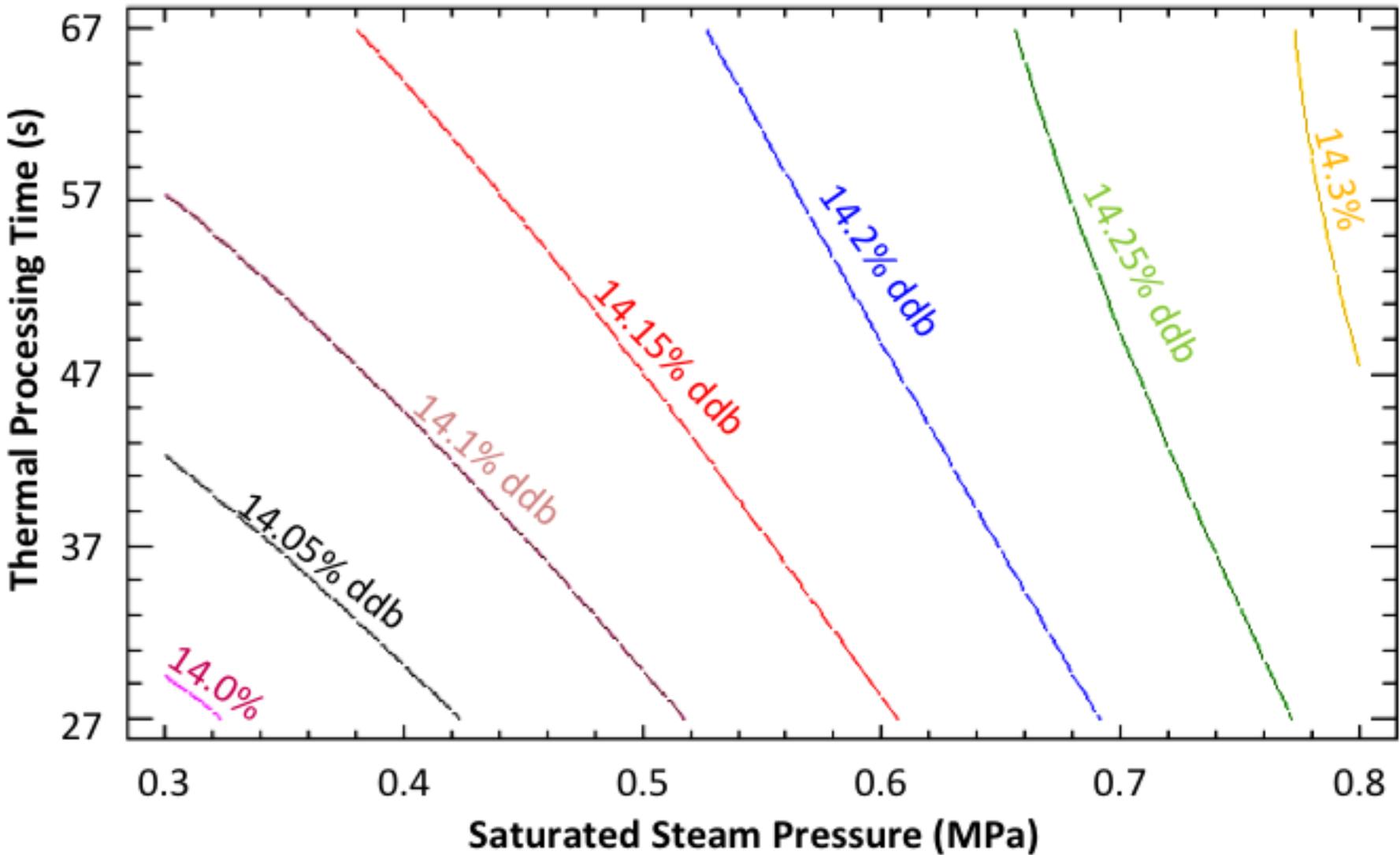
(c)

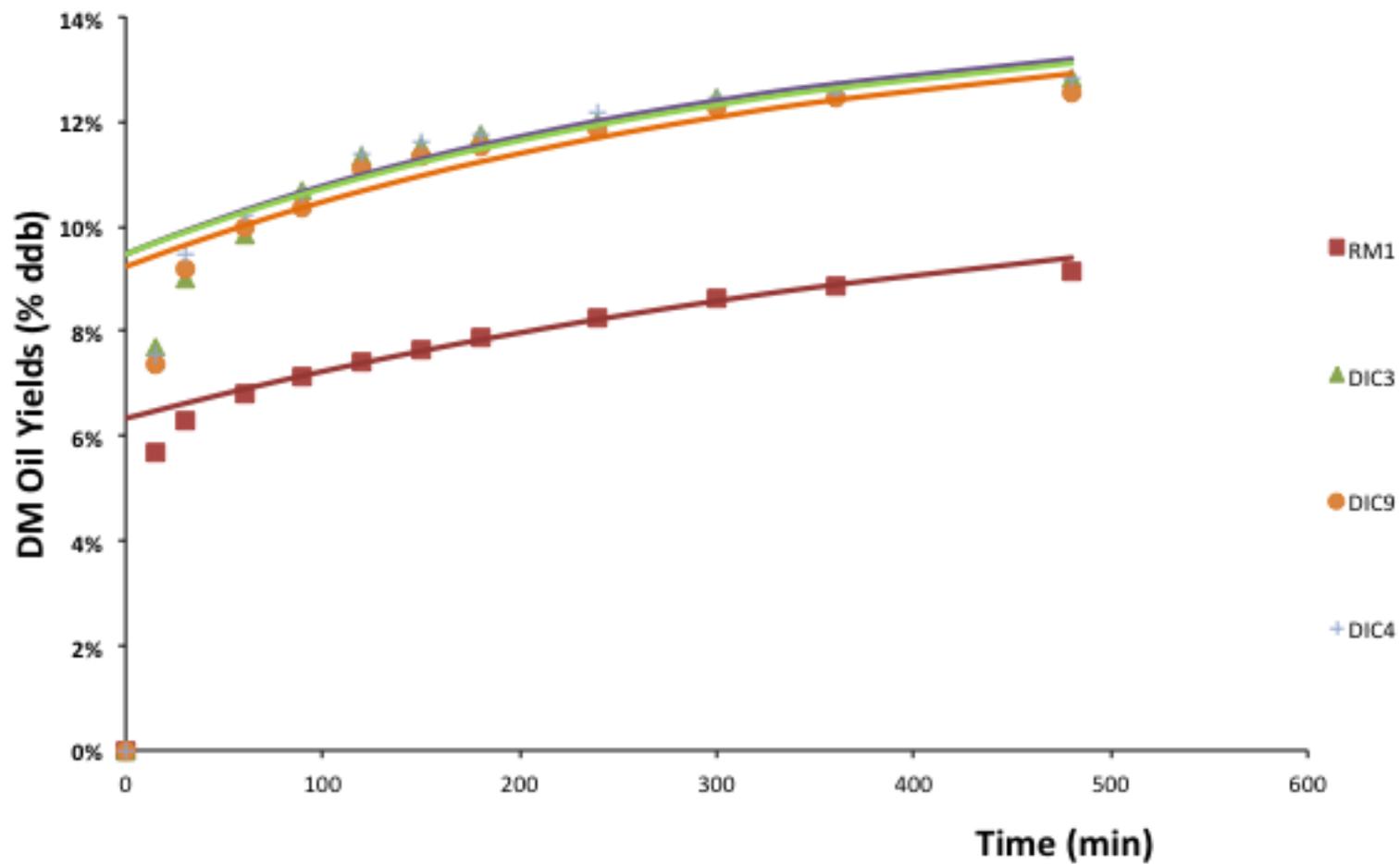
### Estimated Response Surface



D

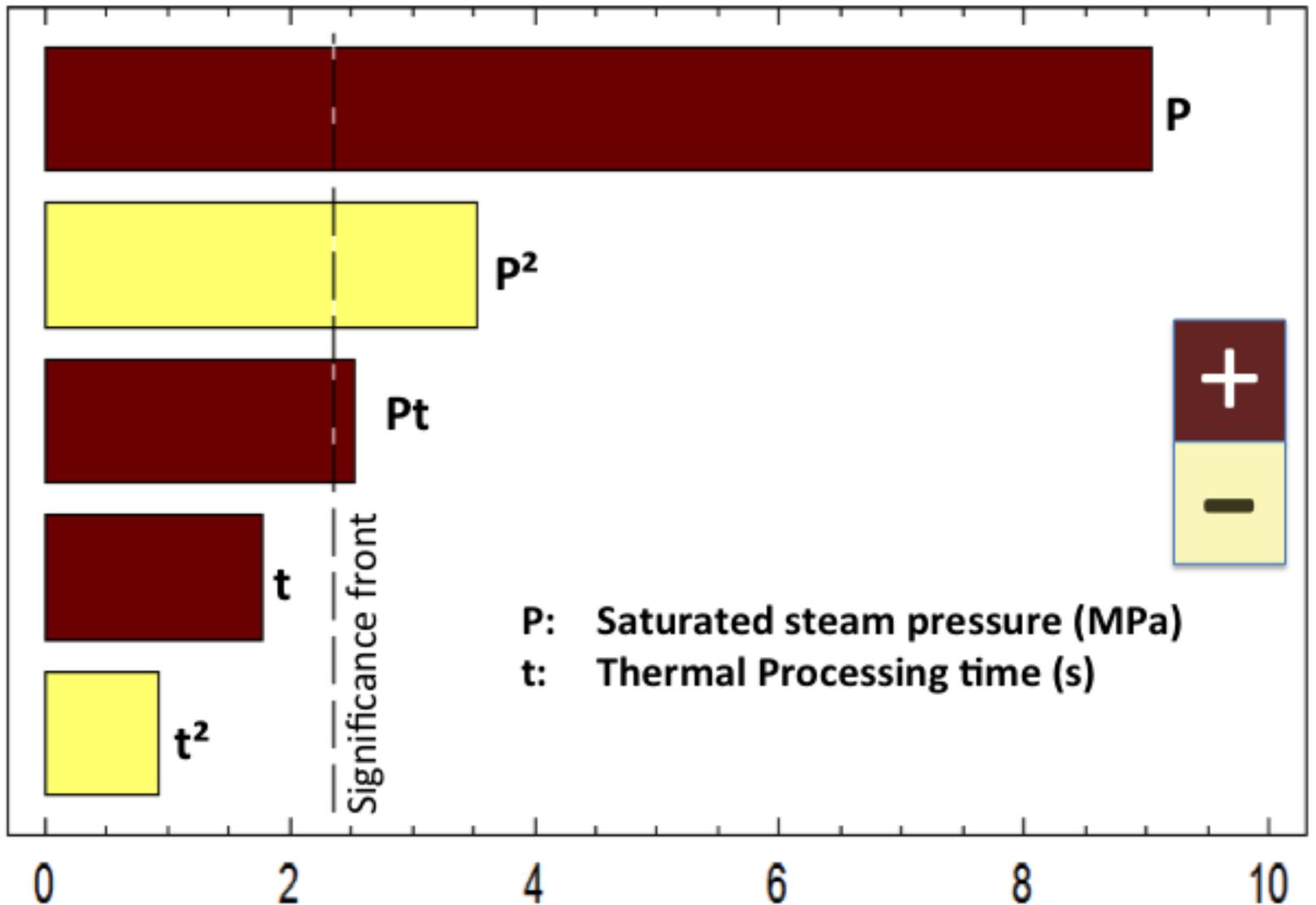
Contours of Estimated Reponse Surface of ASE oil yields (% ddb)





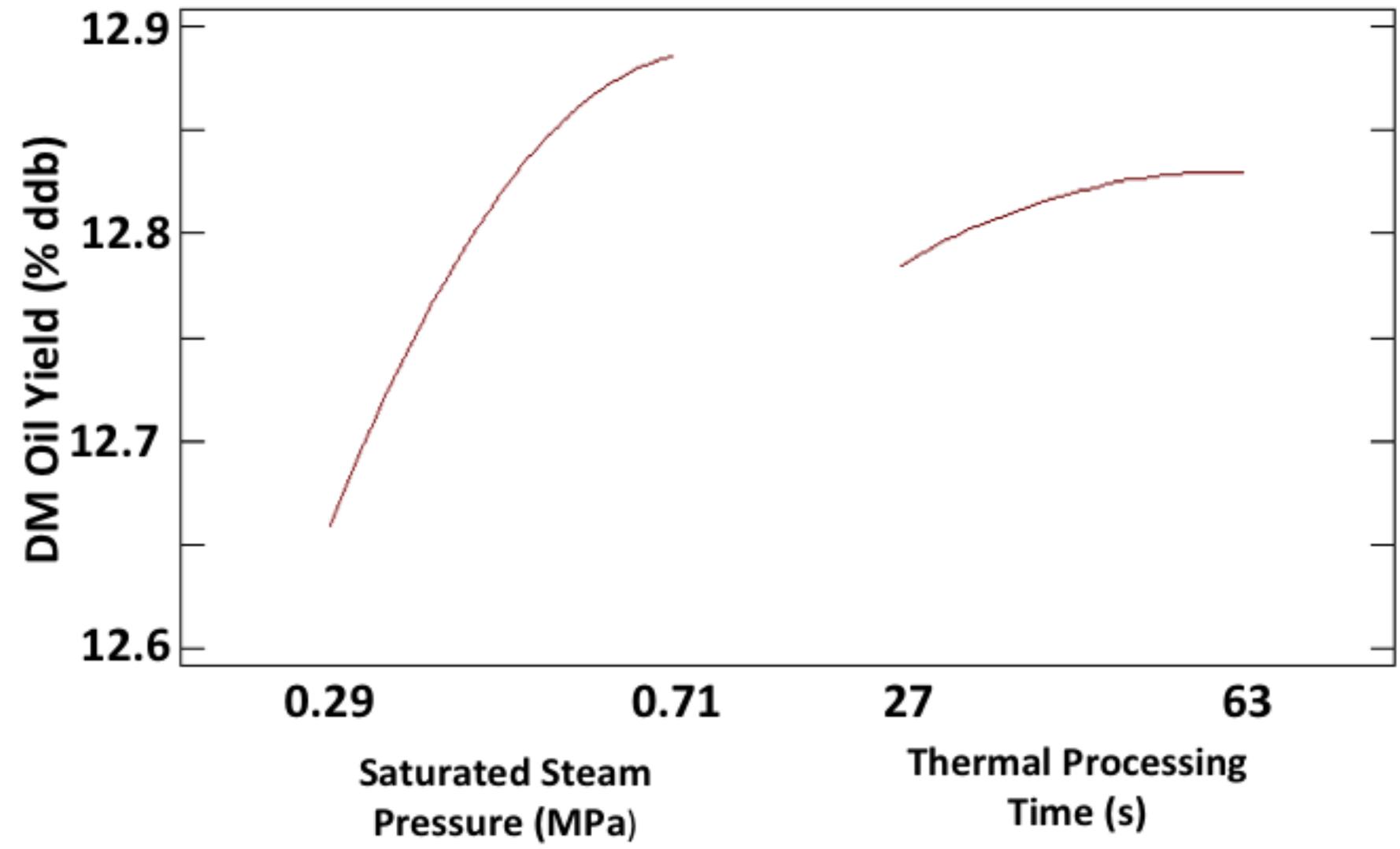
Kinetics of oil extraction from various DIC textured date seed powder

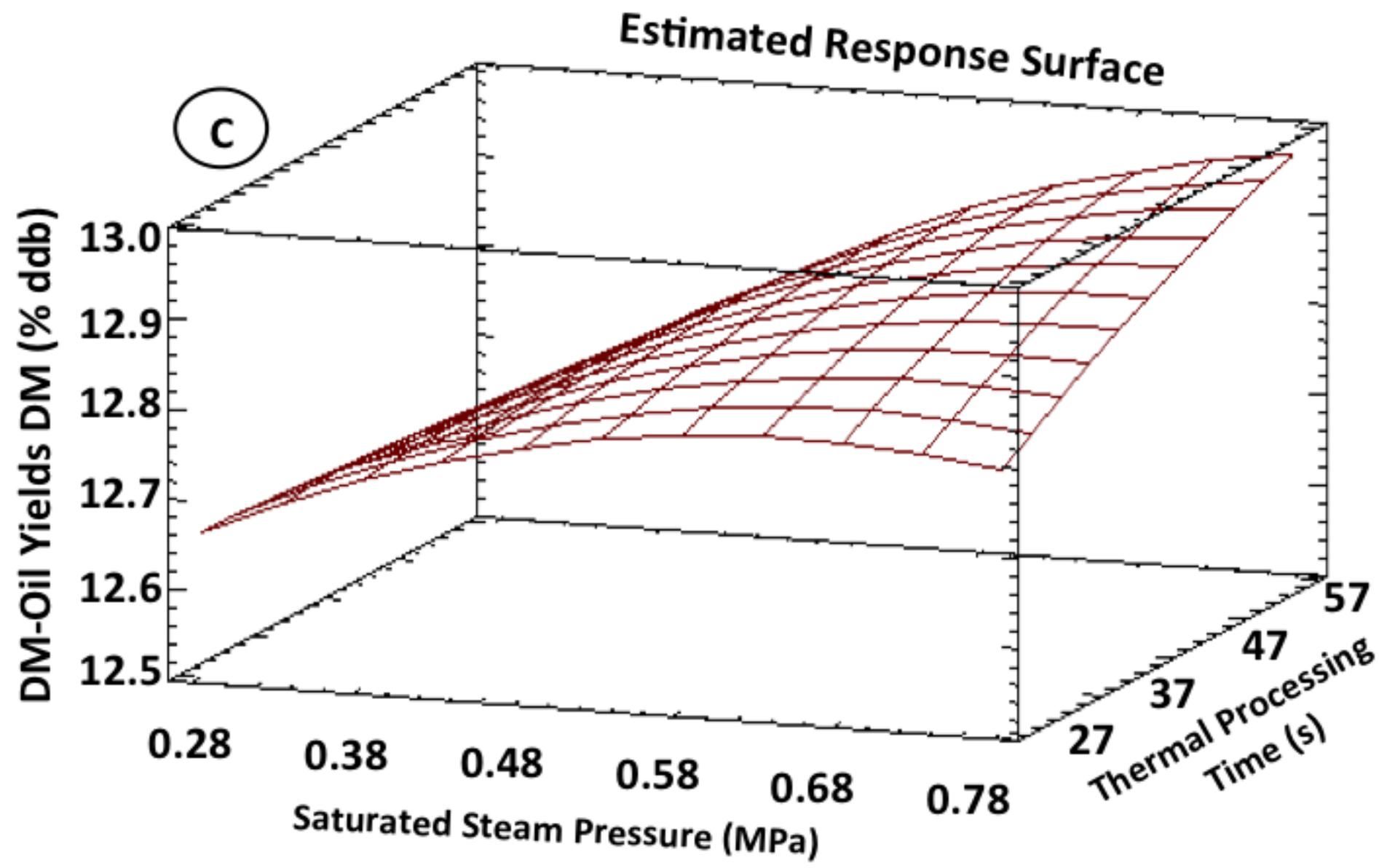
Standardized Pareto Chart for DM oil yield % ddb)



**B**

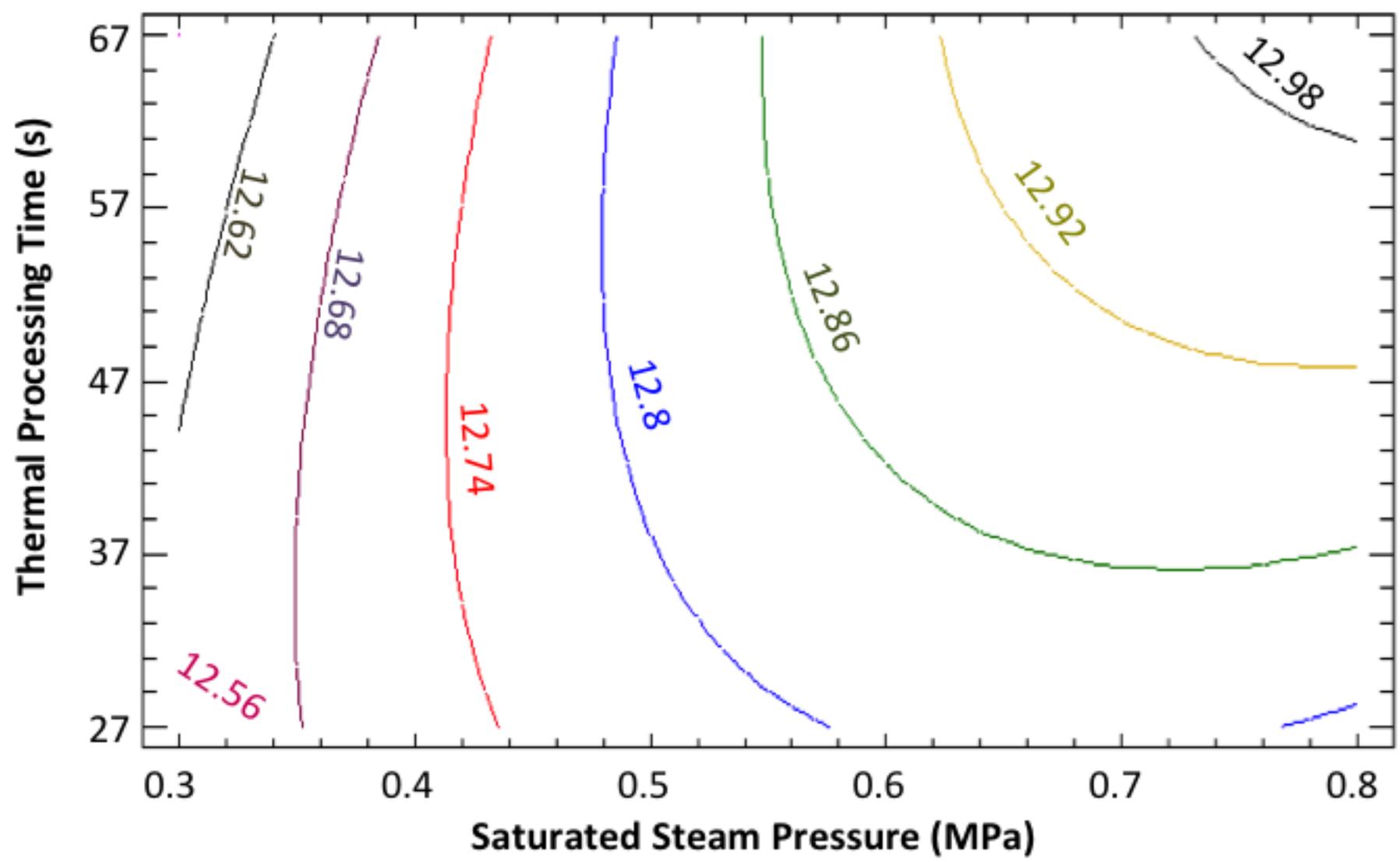
Main Effects Plot for DM oil yields (% ddb)



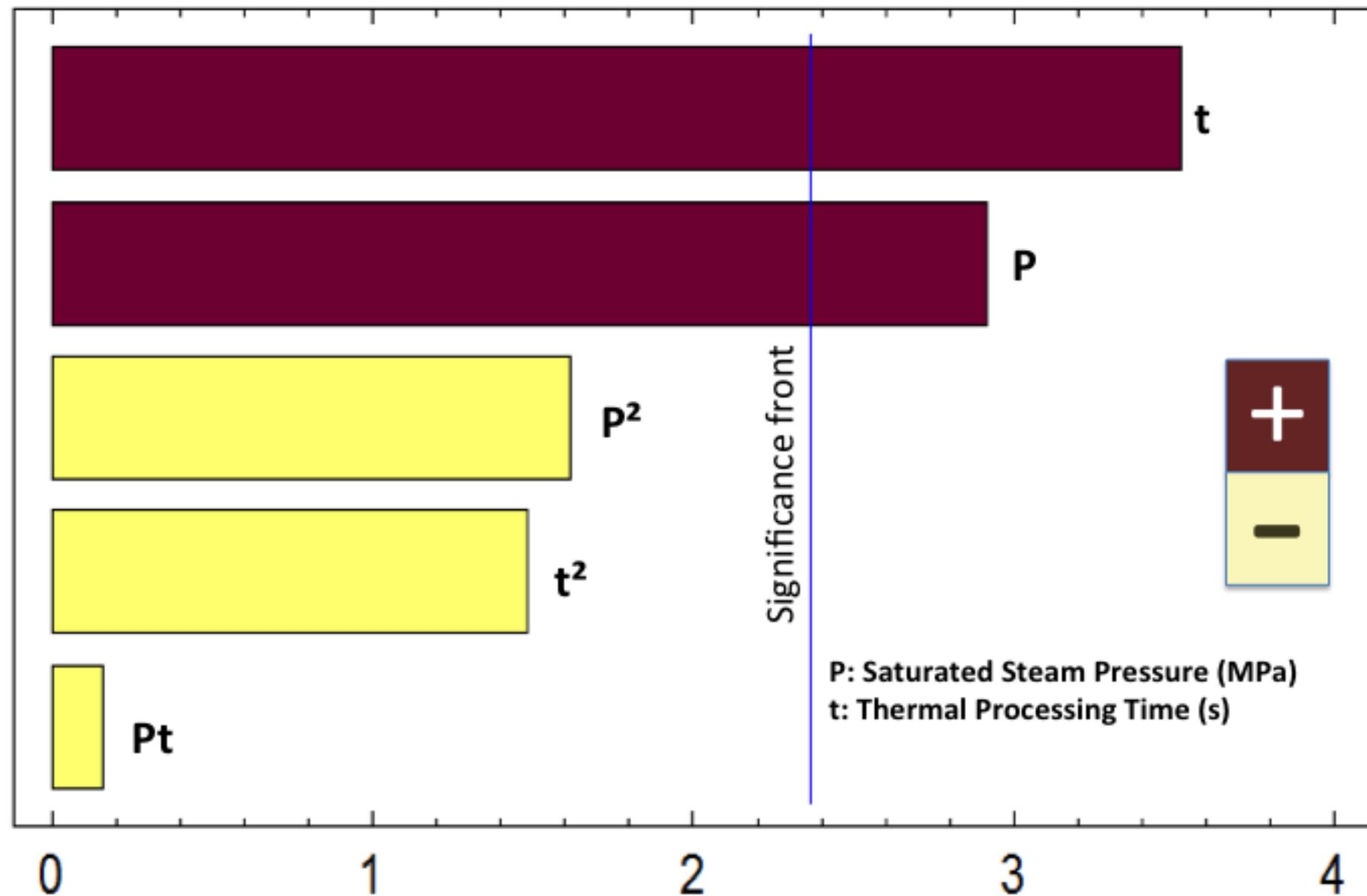


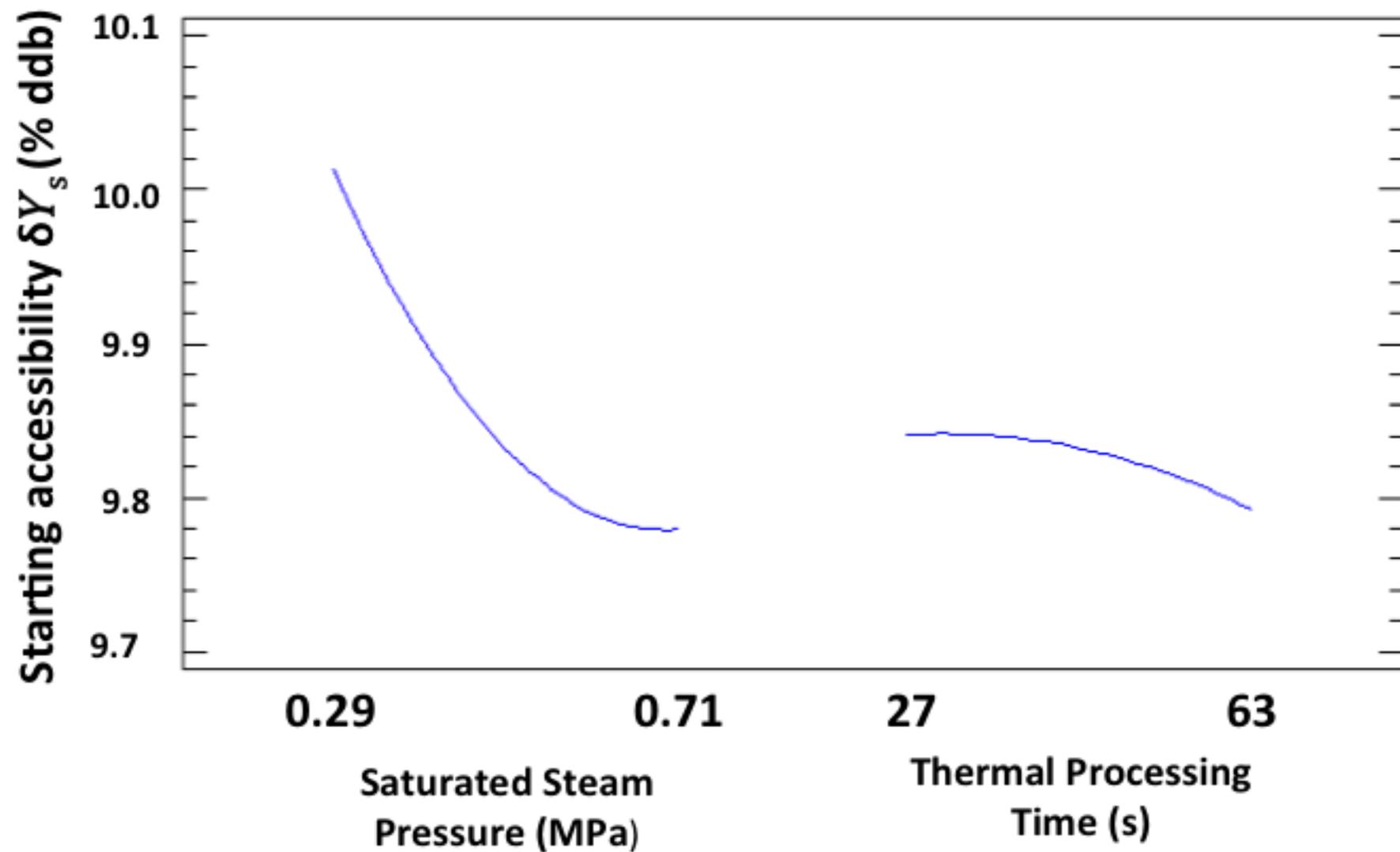
D

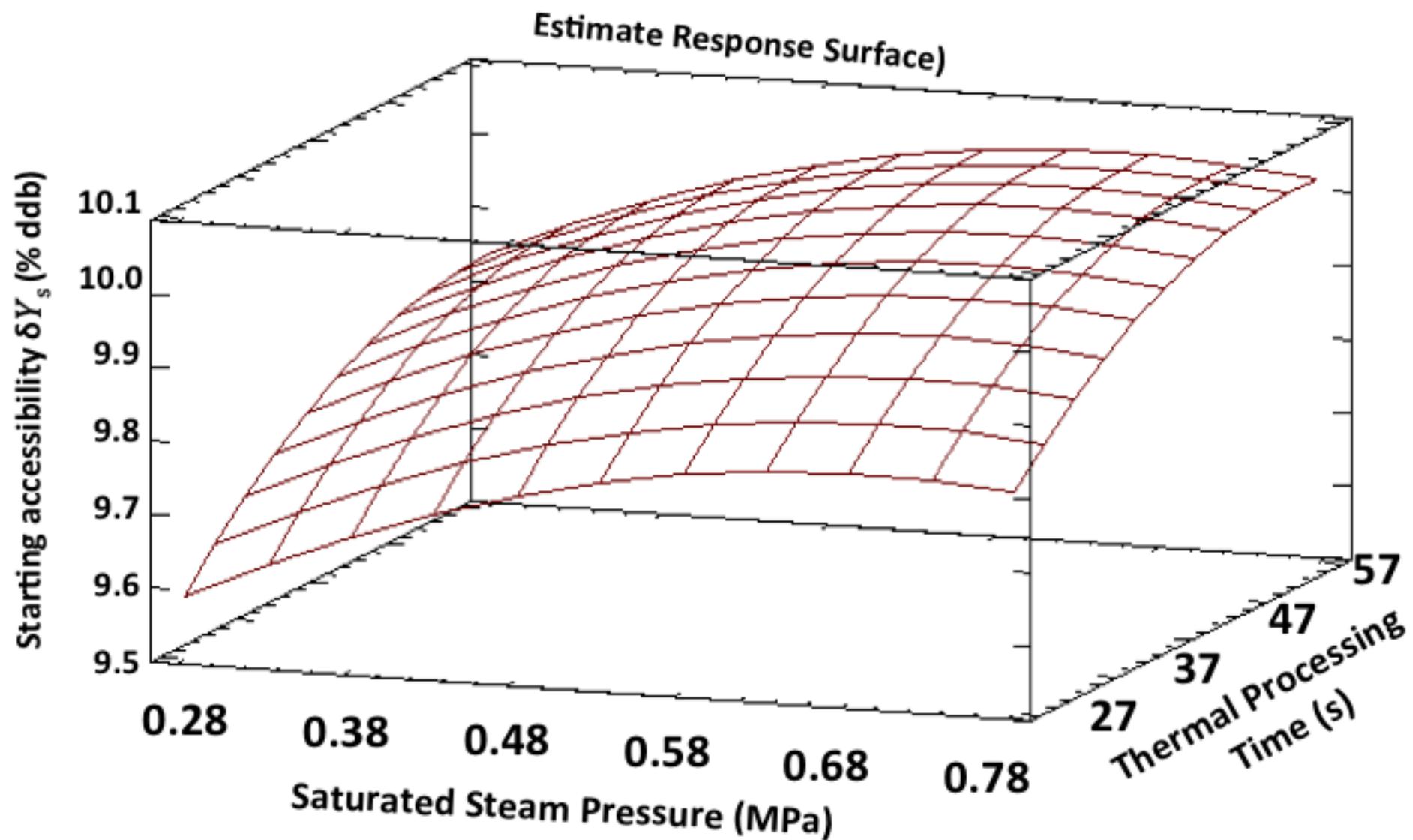
Contours of Estimated Reponse Surface of DM Oil yields (% ddb)



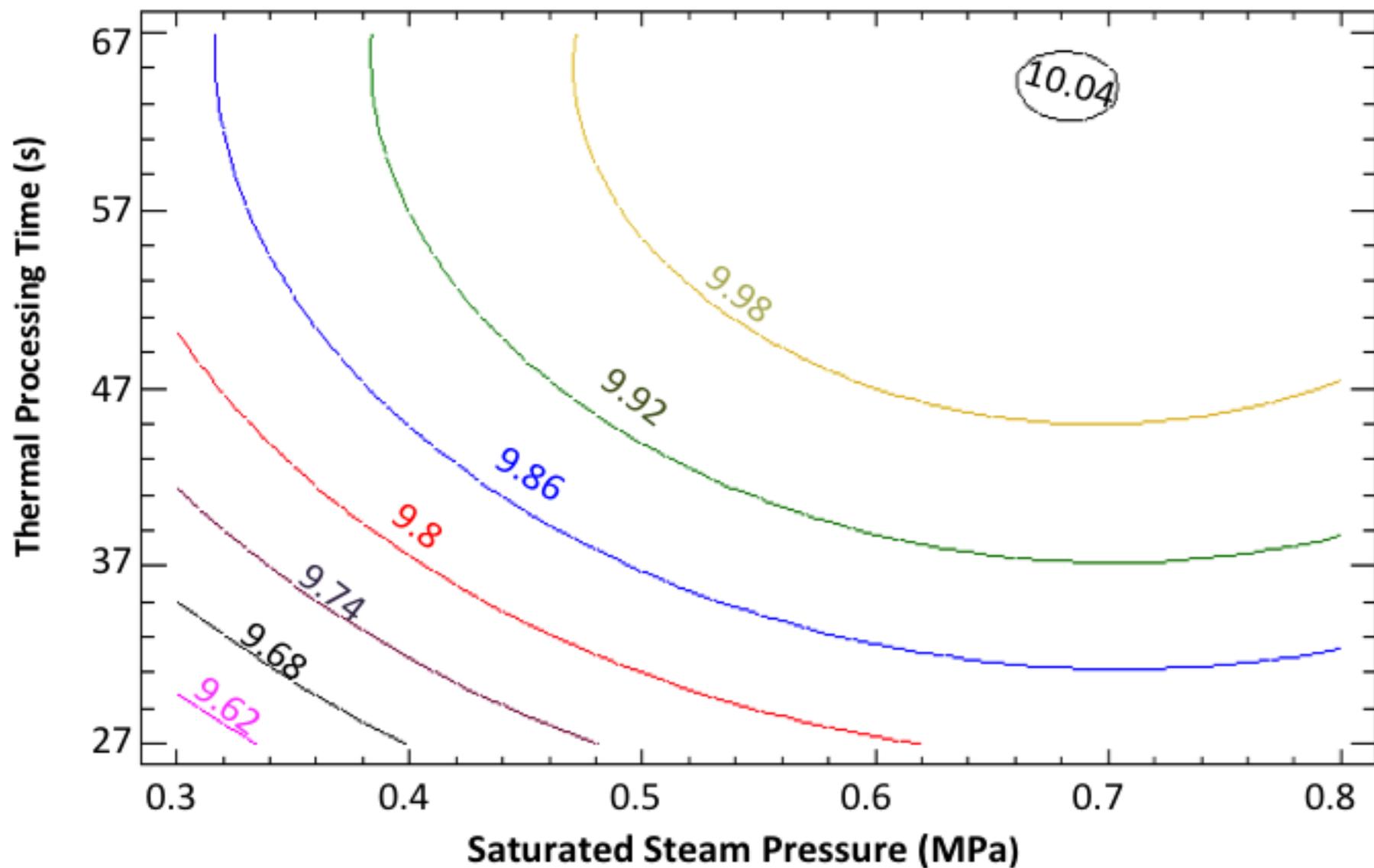
Satndarized Pareto Chart Starting accessibility  $\delta Y_s$  (% ddb)

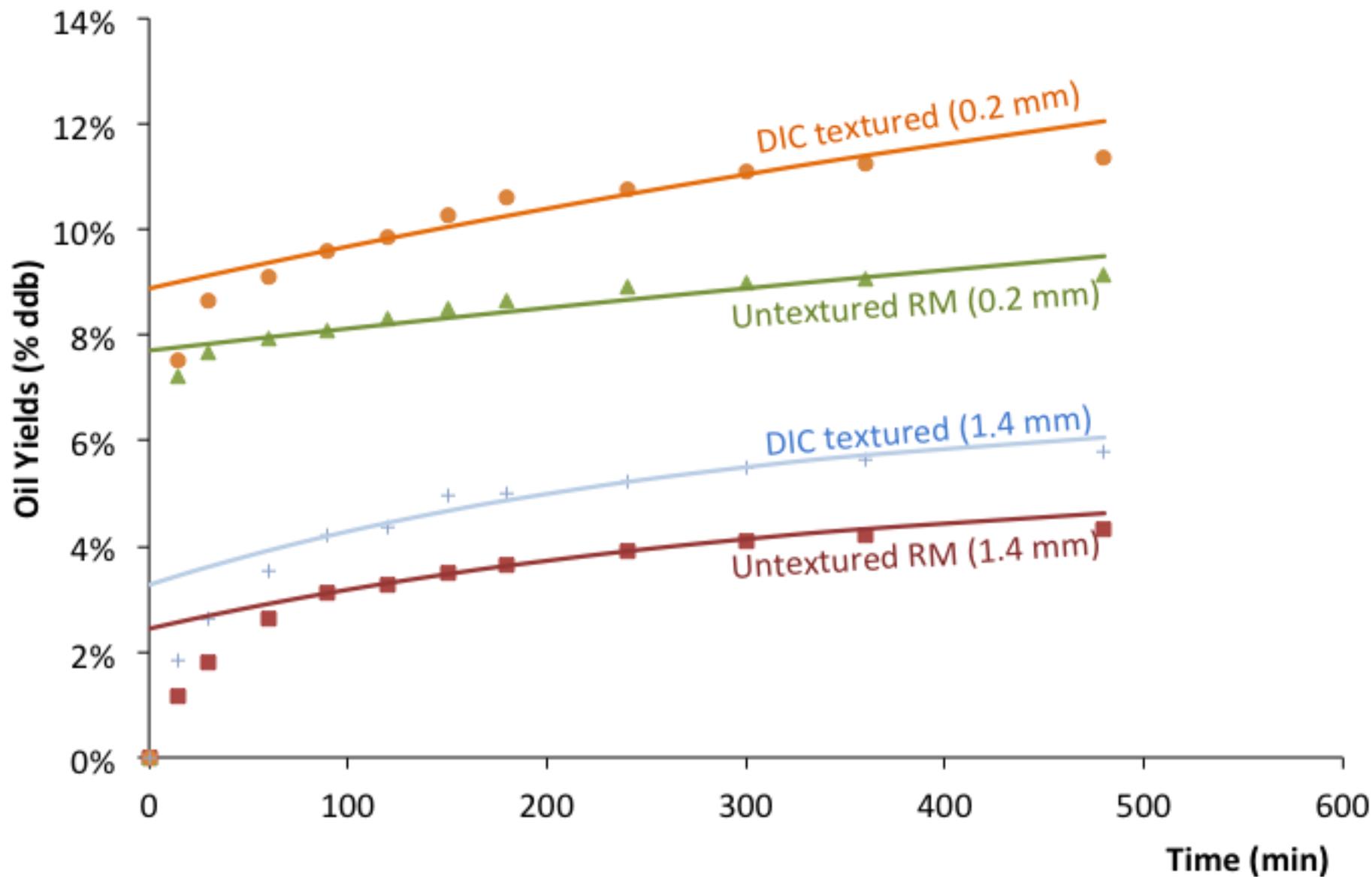


**B****Main Effects Plot for Starting accessibility  $\delta Y_s$  (% ddb)**

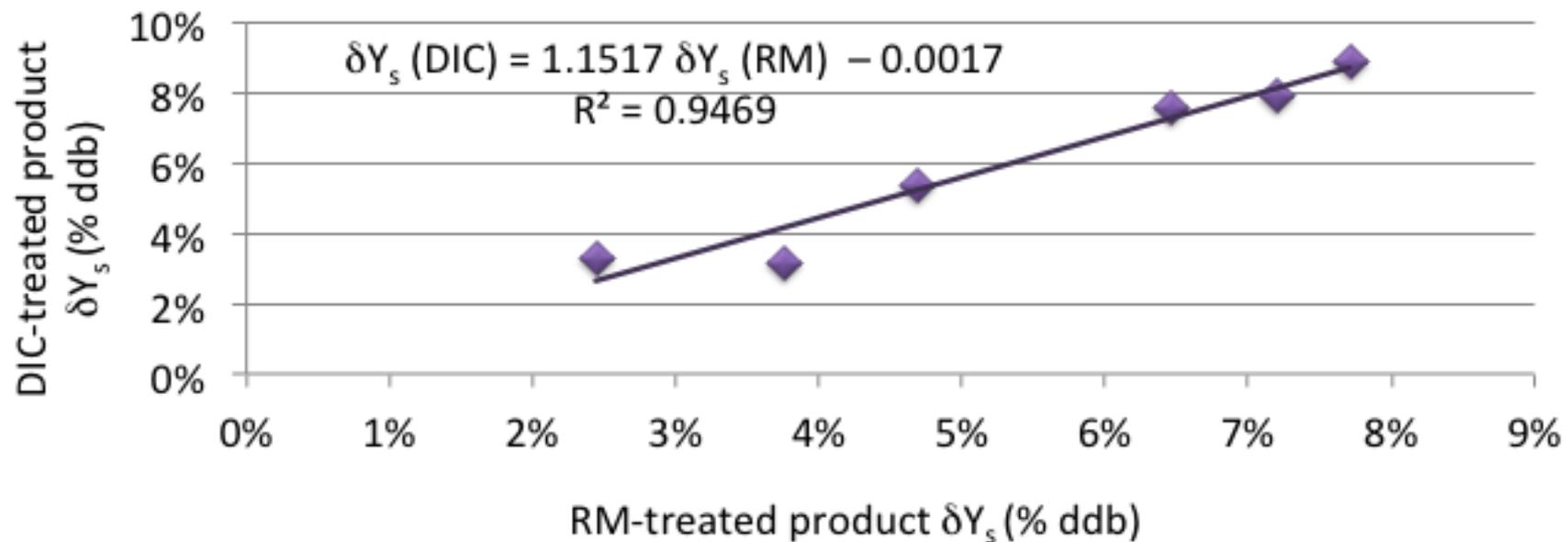
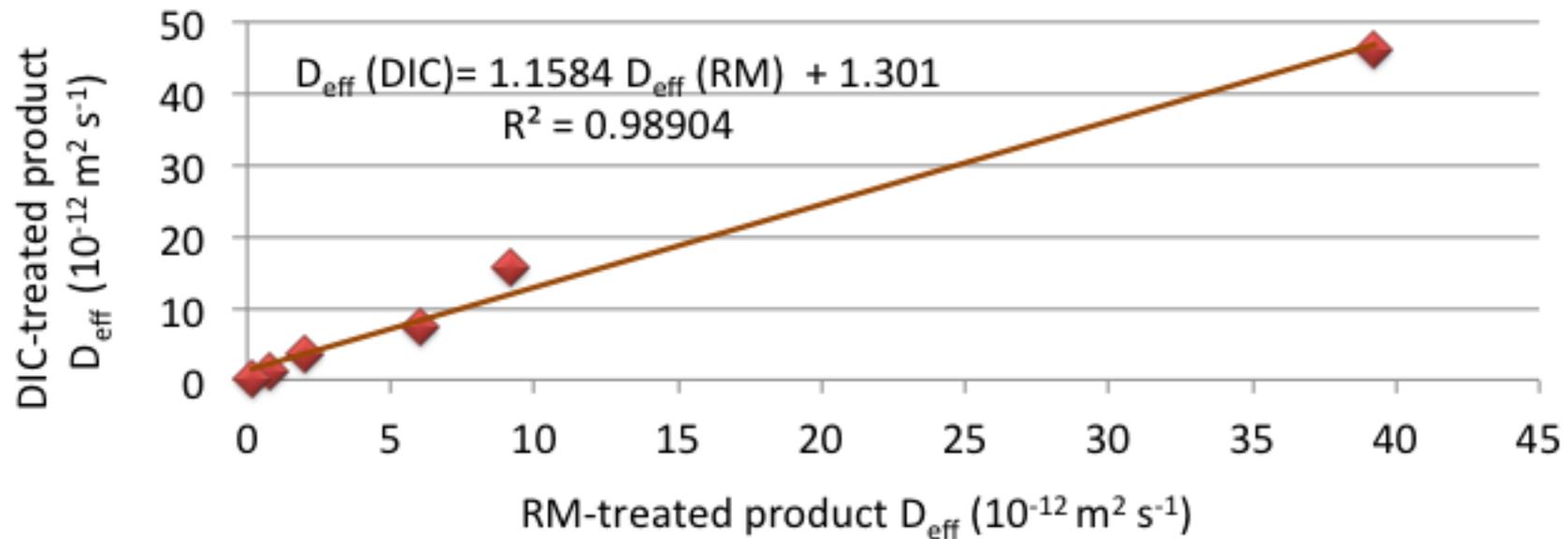


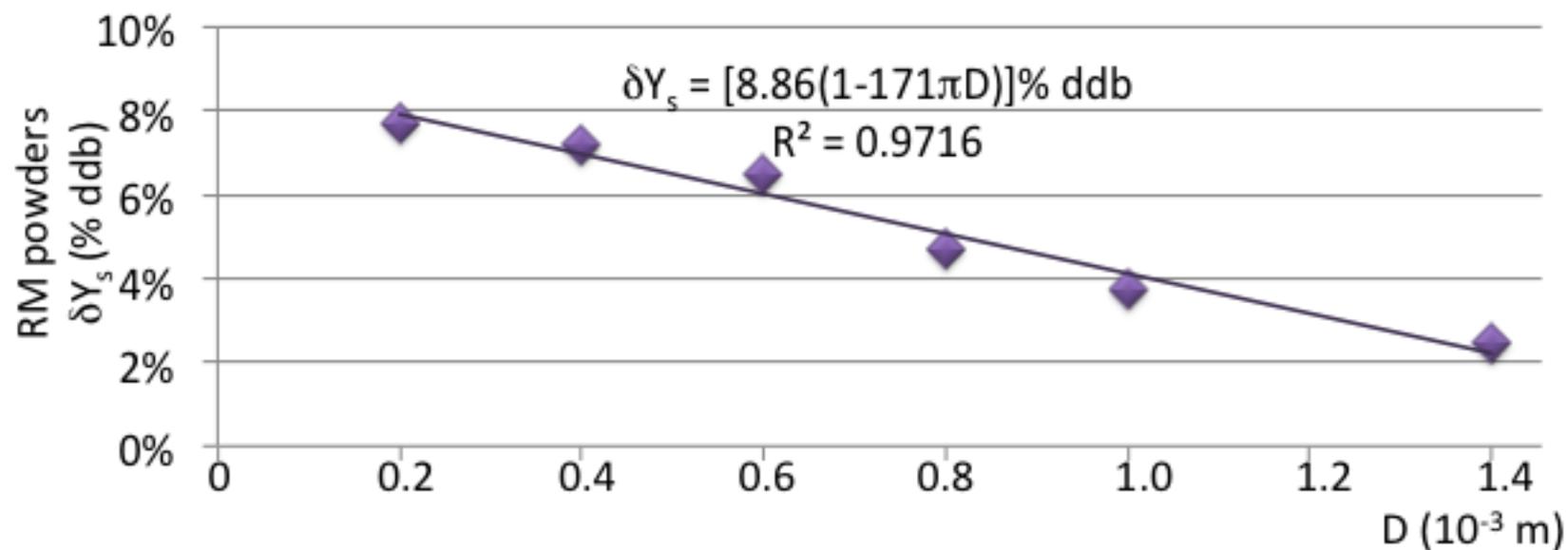
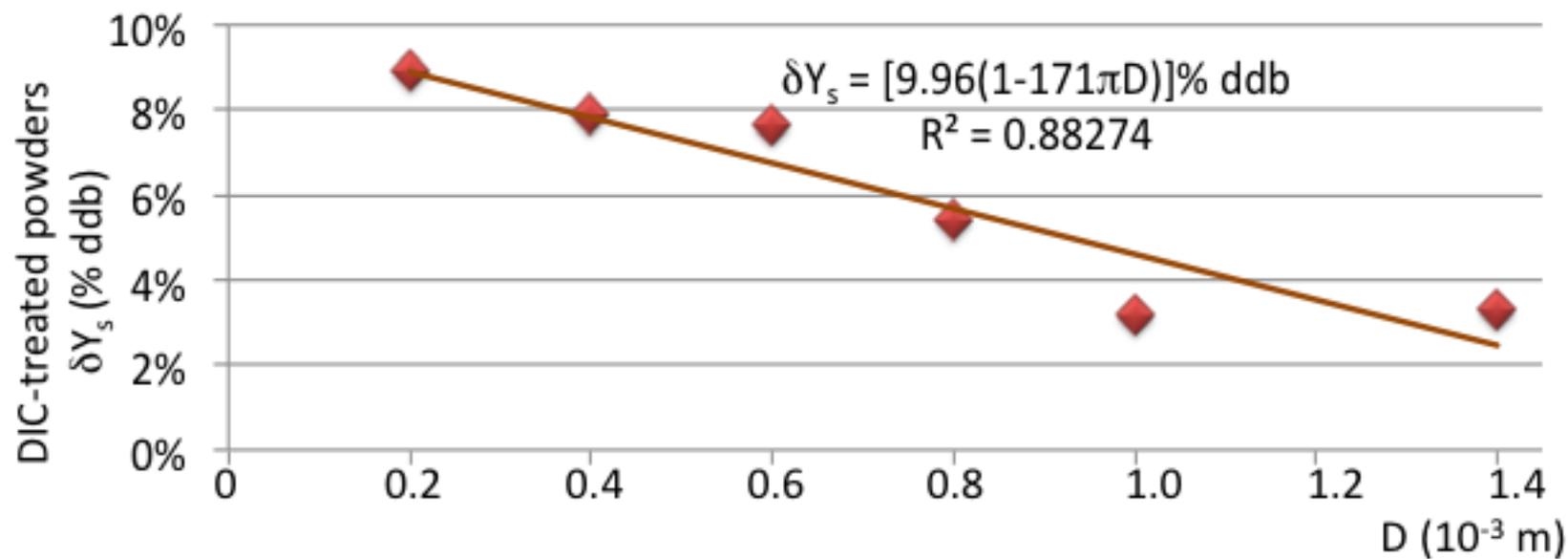
Contours of Estimate Response Surface





Kinetics of oil extraction from different size particle of date seeds





1            Modeling and Intensification of Solvent Oil  
2            Extraction from Date Seeds Coupling Texturing and  
3            Grinding Processes

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4  
5            *Table 1 Independent variable and levels used in Response Surface Methodology RSM Design of*  
6            *Experiments (DoE)*

Coded level	- $\alpha$	-1	0	+1	+ $\alpha$
Saturated Steam pressure (MPa)	0.2	0.29	0.5	0.71	0.8
Processing time (s)	20	27	45	63	70

7            Since we used an orthogonal factorial design,  $\alpha$  is the axial distance:  $\alpha = 1.41421$

8

9

10 *Table 2 Results of date seed oil yields after Accelerated Solvent Extraction ASE and Dynamic*  
 11 *Maceration DM extraction*

Run no	P	t	YASE	YDM2h	RIE	RTO	$\delta Y_s$	Deff
	(MPa)	(s)	(% ddb)	(% ddb)	(%)	(%)	(% ddb)	(10 <sup>-12</sup> m <sup>2</sup> /s)
DIC1; 4; 7; 10; 13	0.5	45	14.154	11.312	0.244	1.000	9.928	9.280
			0.022	0.038	0.005	0.002	0.050	0.160
DIC2	0.8	45	14.25	11.42	25%	101.03%	10.06	8.9
DIC3	0.5	70	14.2	11.31	24%	100.12%	9.86	9.7
DIC5	0.71	63	14.28	11.43	26%	101.03%	10.13	9
DIC6	0.71	27	14.24	11.27	24%	99.76%	9.82	9.1
DIC8	0.29	27	13.97	11.11	22%	98.33%	9.64	10.1
DIC9	0.29	63	14.15	11.1	22%	98.27%	9.57	9.2
DIC11	0.2	45	14.06	11.16	23%	98.74%	9.71	9.2
DIC12	0.5	20	14.08	11.29	24%	99.88%	9.85	9.2
RM	-	-	11.35	7.47	0%	65.81%	6.29	8.7

12 P: Saturated steam pressure (MPa)

13 t: Processing time (s)

14  $Y_{ASE}$  : Yields of extracted oil using ASE (Accelerated Solvent Extraction) (% ddb dry-dry basis)

15  $Y_{DM2h}$ : Yields of extracted oil using Dynamic Maceration (DM) for 2 h (% ddb dry-dry basis)

16 RTO is the **Ratio of Total Oil extraction**:  $RTO = \frac{Y_{DM;2h}}{Y_{ASE;RM}}$ ;

17 RIE is the Ratio of Improvement in total oil Extraction:  $RIE = \frac{Y_{DM;DIC;2h} - Y_{DM;RM;2h}}{Y_{DM;RM;2h}}$ .

18  $\delta Y_s$ : Starting accessibility ((% ddb dry dry basis).

19  $D_{eff}$ : Effective diffusivity (m<sup>2</sup> s<sup>-1</sup>)

20

Table 3. Oil yields from different particle size of date seeds.

Run size (mm)		Yield % ddb				
		$Y_{DM,t=2h}$	$Y_{DM,t=8h}$	$Y_{ASE}$	RTO	RIE
0.2	DIC	11.62	13.39	15.20	102%	22%
	RM	9.54	10.49	12.69	84%	
0.4	DIC	10.75	12.70	14.45	95%	21%
	RM	8.89	9.55	11.94	78%	
0.6	DIC	10.27	11.58	13.75	90%	32%
	RM	7.79	8.25	10.38	69%	
0.8	DIC	7.94	9.87	12.43	70%	30%
	RM	6.1	7.24	9.49	54%	
1	DIC	5.45	8.51	10.19	48%	16%
	RM	4.7	5.52	7.6	41%	
1.4	DIC	4.67	6.19	6.71	41%	35%
	RM	3.47	4.57	5.32	31%	

24 *Table 4. Starting accessibility  $\delta Y_s$ , effective diffusivity  $D_{eff}$ , and oil yield after 2 h DM extraction*  
 25  *$Y_{t=2h}$  for 1.4 mm and 0.2 mm particle sizes.*

D (mm)	1.4	1	0.8	0.6	0.4	0.2
RM $\delta Y_s$ (% ddb)	2.53%	4.06%	5.15%	7.21%	8.16%	8.77%
DIC $\delta Y_s$ (% ddb)	3.33%	3.62%	6.01%	8.73%	9.01%	10.29%
RM $D_{eff}$ ( $10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	47	11.1	7.9	3.6	1.5	0.4
DIC $D_{eff}$ ( $10^{-12} \text{ m}^2 \text{ s}^{-1}$ )	62.4	20.8	10.6	5.8	2.9	0.7

26

27

Table 5. Fatty acid profile (relative %) obtained via gas chromatography

%	Fatty acid profile (relative %) of seeds date			
	RM (F)	DIC (F)	RM (DN)	DIC (DN)
C8:0	-	0.30	0.18	0.32
C10:0	-	0.37	0.23	0.38
C12:0	15.64	23.84	18.32	21.68
C14:0	7.36	8.78	8.24	9.14
C16:0	9.65	8.13	10.72	8.44
C16:1	0.27	-	-	-
C18:0	3.29	2.56	2.77	2.78
C18:1	53.14	47.81	44.88	49.40
C18:2	10.28	7.69	14.29	7.45
C20:0	0.36	0.31	-	-
C22:0	-	0.21	0.37	0.41
Saturated fatty acid (SFA)	36.22	44.5	40.83	43.15
Mono-unsaturated fatty acid (MUFA)	53.41	47.81	44.88	49.40
Poly-unsaturated fatty acid (PUFA)	10.28	7.69	14.29	7.45

DN: Deglet Nour variety      F: Ftimi variety