11. stručni skup

FUNKCIONALNA HRANA U HRVATSKOJ

AGRO-OTPAD KAO IZVOR BIOAKTIVNIH SASTOJAKA

izv. prof. dr. sc. Stela Jokić

Zagreb, 04.07.2018.

Veliki interes u iskorištenju nusproizvoda prehrambene industrije

PREHRAMBENA INDUSTRIJA

→ **maksimalno iskorištenje sirovine prilikom proizvodnje**

→ **uz minimalnu količinu otpada**

nusproizvod ili sirovina u nekom budućem procesu

→ **raste svijest ljudi o potrebi zaštite okoliša**

→ **zelene i održive tehnologije**

NUSPROIZVODI PREHRAMBENE INDUSTRIJE

NUSPROIZVODI PREHRAMBENE INDUSTRIJE – actual & future research

Unutarnje pregrade oraha

Kakao ljuska

Komina grožđa (sjemenke i kožica)

Koštice marelice

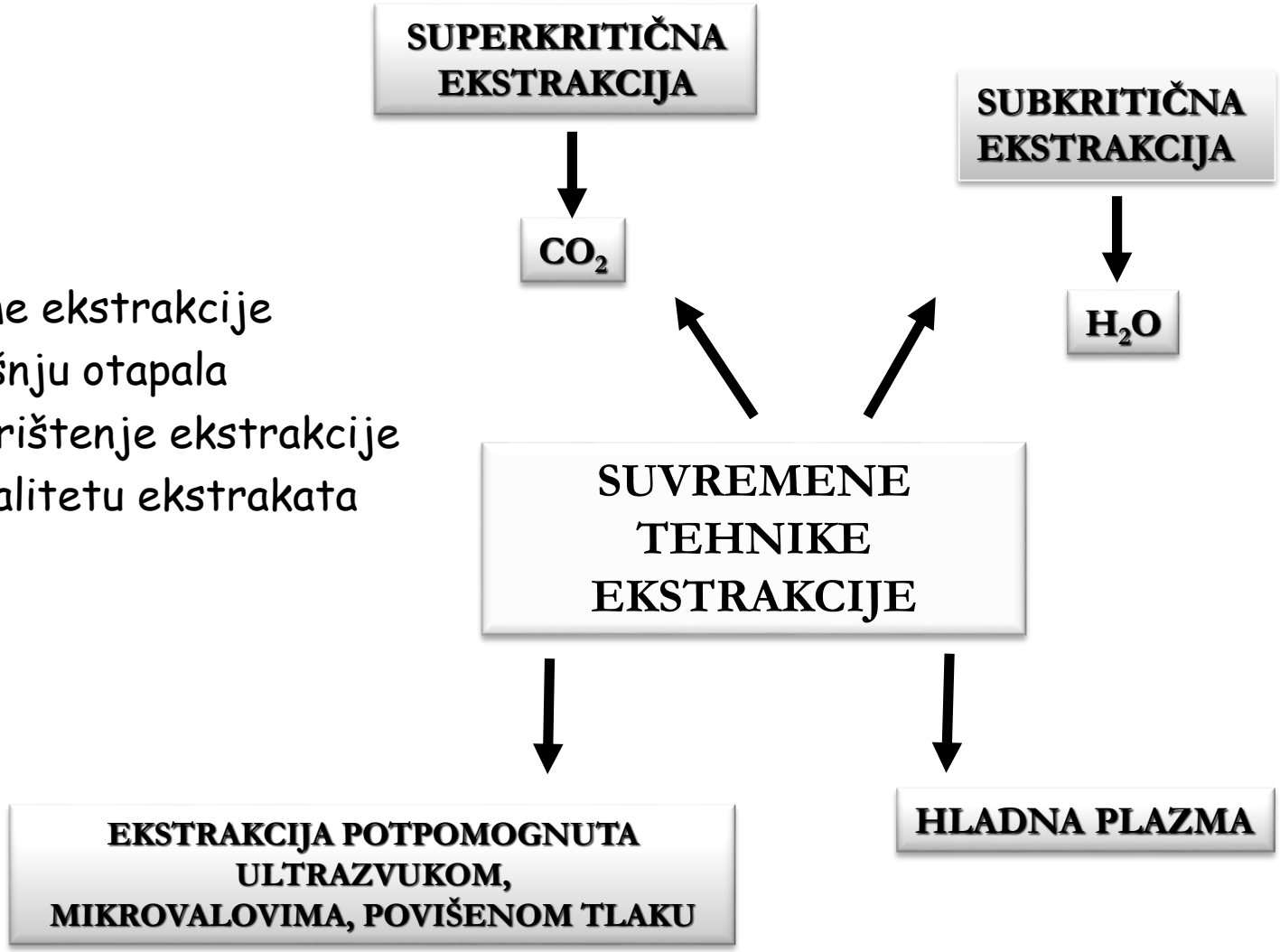
Pljevica kave

Koštice trešnje

Kora nara

Zašto suvremene tehnike ekstrakcije?

- smanjuju vrijeme ekstrakcije
- smanjuju potrošnju otapala
- povećavaju iskorištenje ekstrakcije
- poboljšavaju kvalitetu ekstrakata



HRZZ project: Application of food industry by-products in development of functional and environmentally friendly extruded food products and additives (2014-2018)

„Zero waste" approach

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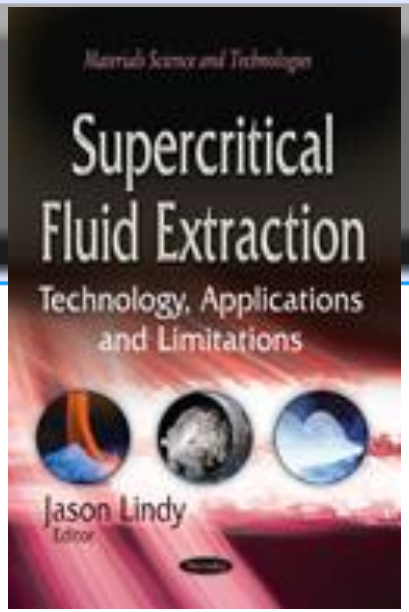
SUPERCRITICAL CO_2 EXTRACTION PILOT PLANT DESIGN – TOWARDS IoT INTEGRATION

Goran Horvat, Krunoslav Aladić, Stela Jokić

Preliminary communication

The interest in high pressure technology during last decades increased intensively. Supercritical Fluid Extraction (SFE) is a process that is growing in importance as an alternative to conventional separation processes. SFE uses environmentally friendly CO_2 as the extracting agent in the process because of its relatively low critical pressure (7,38 MPa), its low critical temperature (304 K), its non-dangerous character and low cost. During this process it is necessary to use high pressures in the procedure. The extractor vessel (pressure vessel) is the most important equipment of the system, where the supercritical conditions need to be established and the extraction occurs. Also other devices (separator vessel, heat exchangers, valves etc.) are necessary to be involved in the process due to used high pressures. Safety is the most important factor while dealing with SFE systems and the design of such equipment with full safety of process is very hard task. Therefore, to achieve the high desired safety level, a reliable control system must be designed as the control system and data communication segment. Various different process parameters such as CO_2 mass flow rate, extraction pressures and temperatures affect the extraction process and the quality of the extract; hence these parameters need to be precisely controlled and monitored during the extraction. A design of one supercritical CO_2 extraction laboratory-pilot plant and development of a remote control and its supervision system is presented in this paper. The developed SFE system (mechanical and electrical components) was compared with the existing commercial systems and its main advantages over the existing systems are presented. By enabling remote control and supervision the classical process control is joined with the concept of Internet of Things (IoT), where the information becomes omnipresent in the vast realm of Internet.

Keywords: *embedded system; process control; supercritical fluid extraction; system construction.*



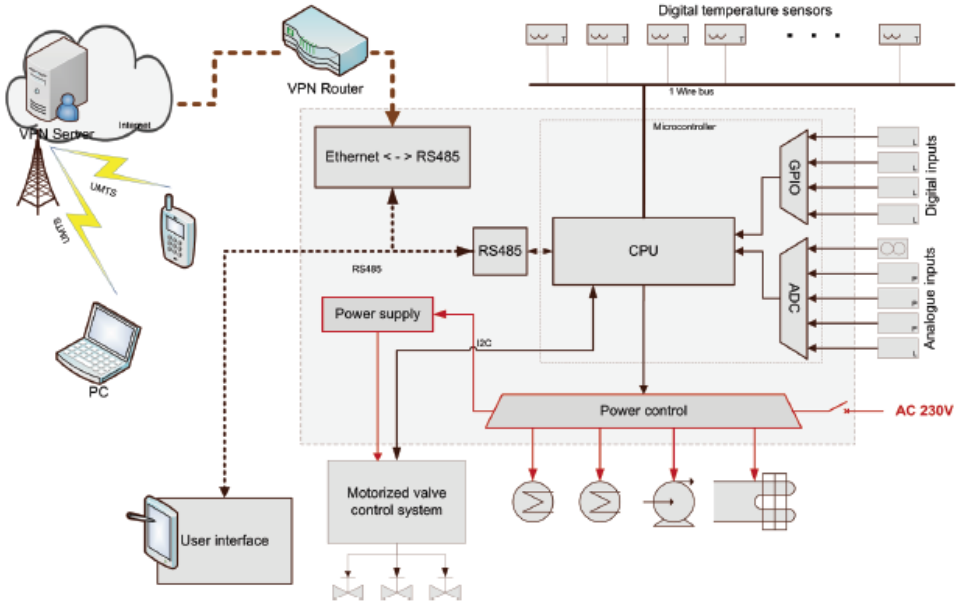


Figure 2 Block diagram of the supporting electronic system

Projektiranje pilot postrojenja za ekstrakciju superkritičnim CO_2 – Prema integraciji s Internetom objekata (IoT)

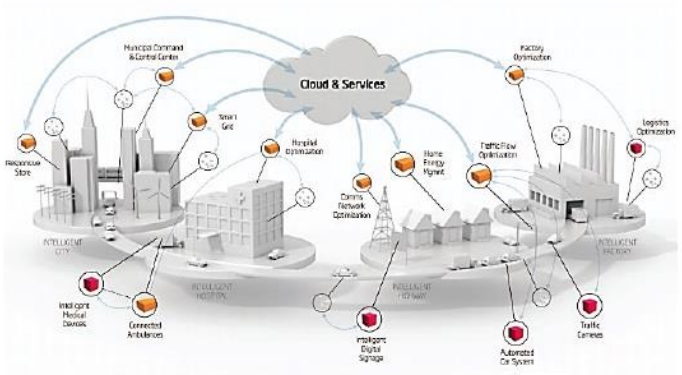
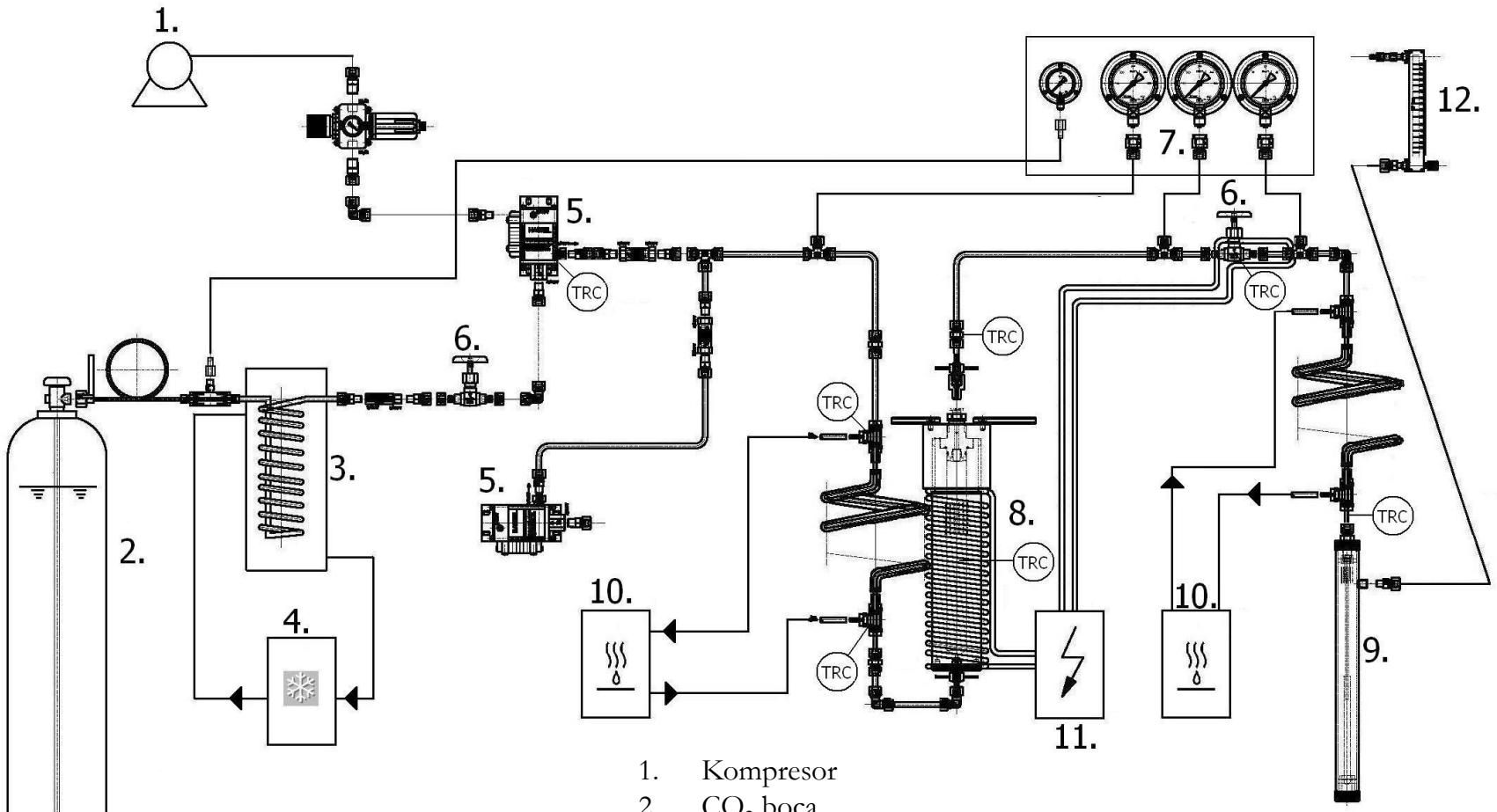
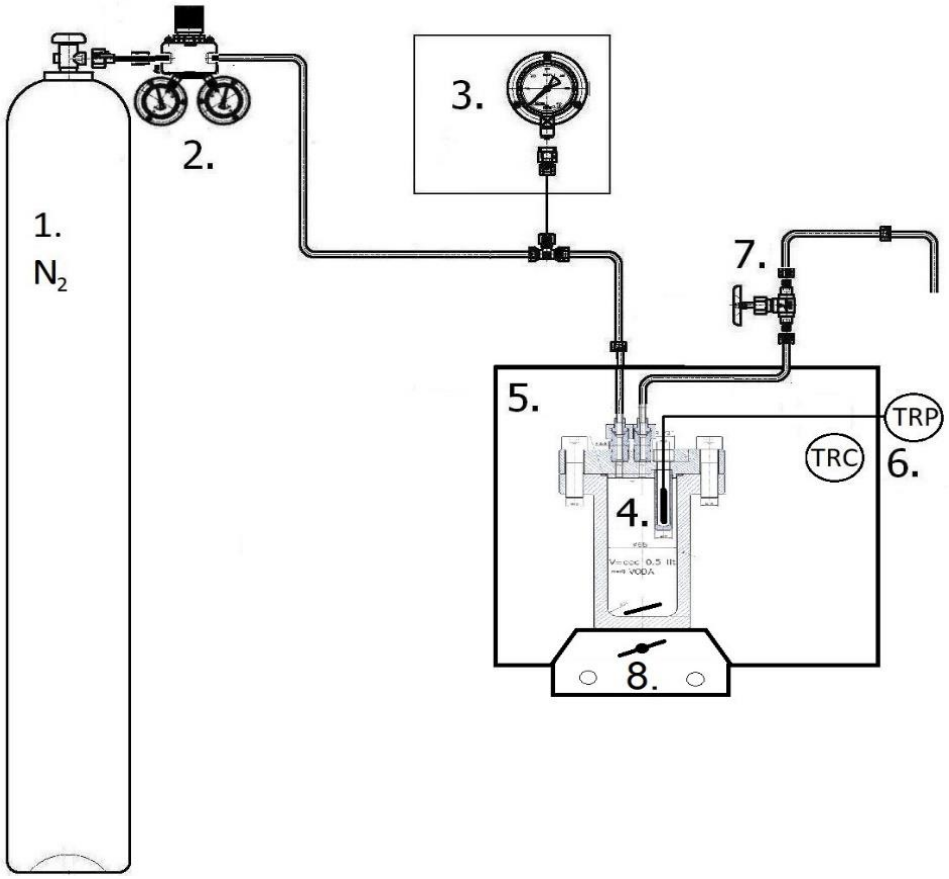


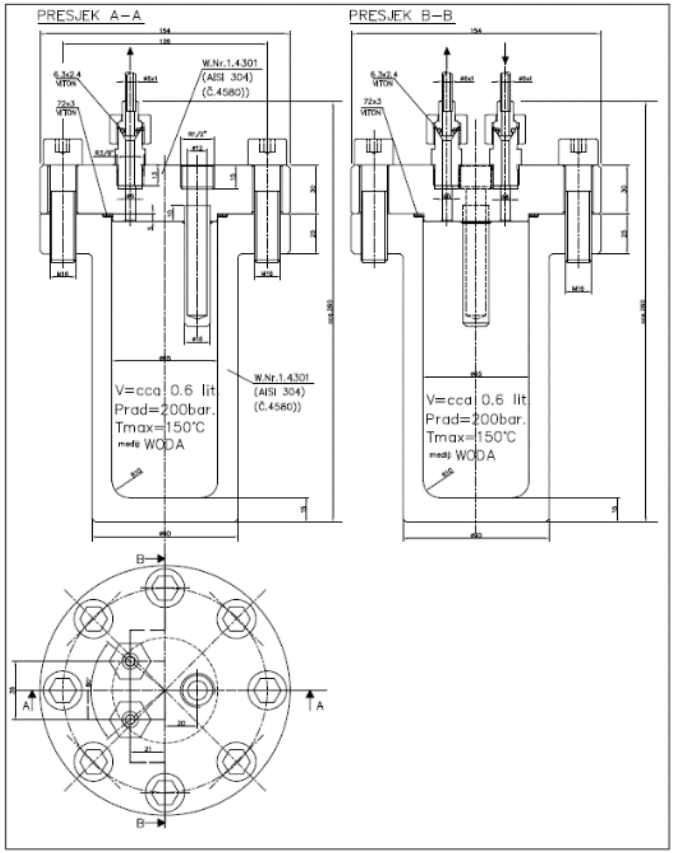
Figure 7 The concept of Internet of Things



1. Kompresor
2. CO_2 boca
3. Visokotlačna zavojnica
4. Rashladna kupelj
5. Visokotlačna pumpa
6. Visokotlačni ventil
7. Manometri
8. Ekstraktor
9. Separator
10. Vodena kupelj
11. Centralizirani sustav grijača
12. Mjerač protoka CO_2

SUBCRITICAL WATER EXTRACTION





(1) N_2 tank (2) Regulator N_2 20/5 MPa (3) Manometer 0-20 MPa (4) Extraction vessel 20 MPa, 200°C (5) Oven 20-300°C (6) TRC - Temperature regulator controller; TRP - Temperature regulated probe (7) High pressure needle valves (8) Magnetic stirrer

Primjer – pogača konoplje

Cannabis sativa L.
(Fedora 17 type)

„Zero waste" approach

Sjemenke konoplje

Pogača nakon prešanja

Pogača nakon SFE

Ekstruzija

Snack proizvodi

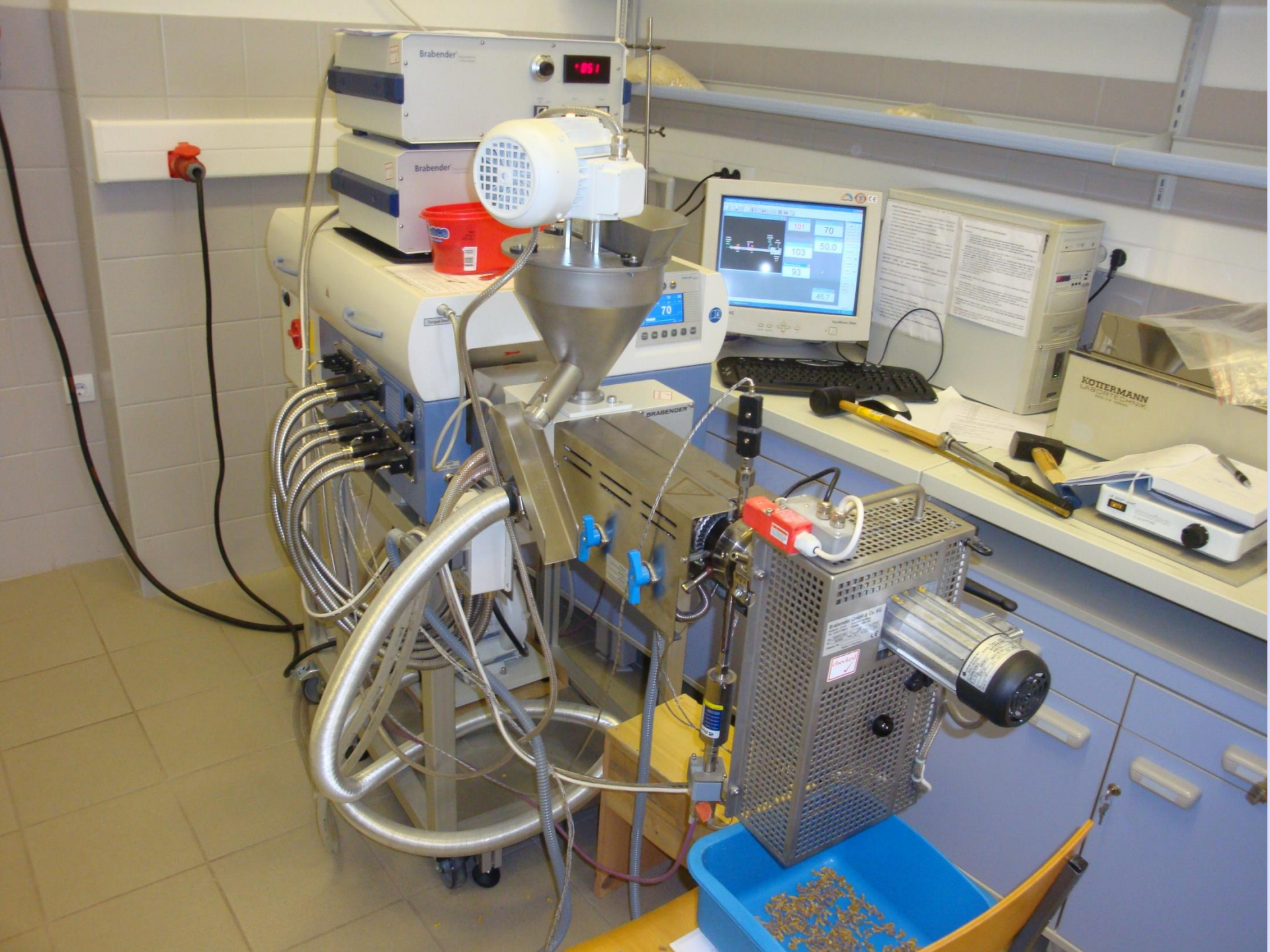
SFE

Pogača (ID 12, 9 and 6 mm)

SFE

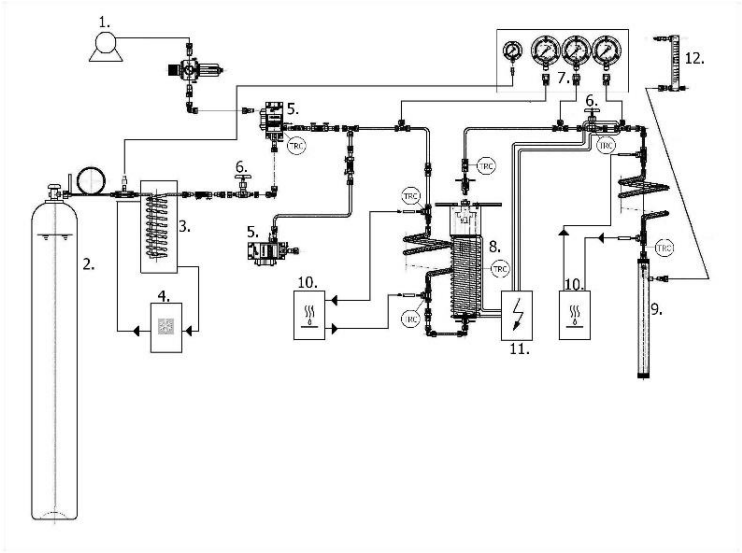
HLADNO PREŠANJE

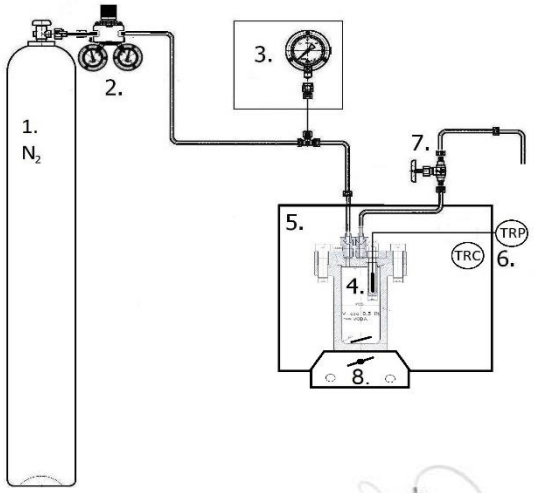
T-temperatura zagrijavanja glave preše
F-frekvencija elektromotora
N-veličina otvora pužne preše


Brabender
Brabender
BRABENDER
KOTTERMANN

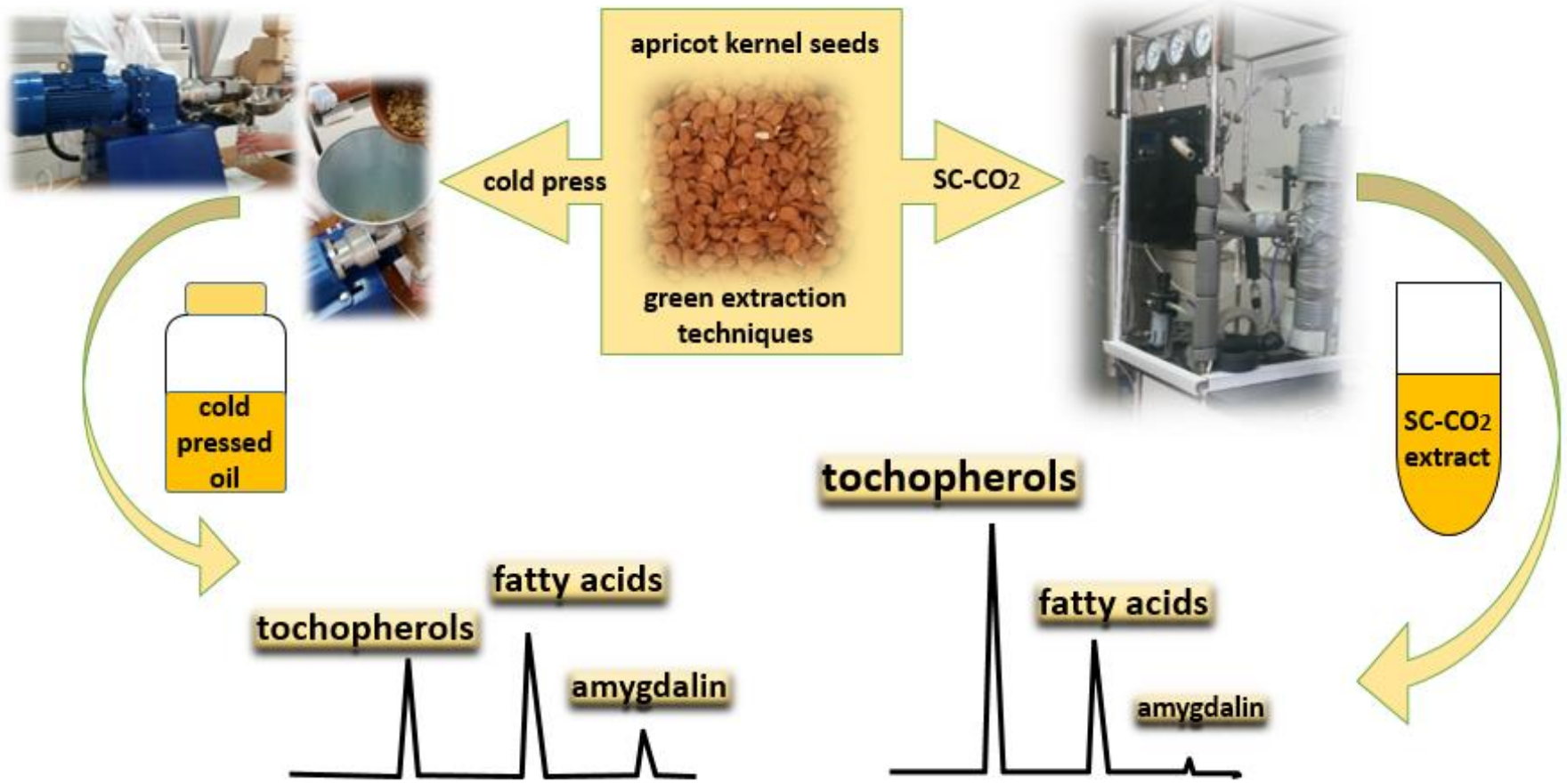
Materijal	Parametri ekstrakcije						Ciljana tvar ili proizvod	Referenca
	Temperatura (K)	Tlak (MPa)	Vrijeme (h)	Protok otapala (g/min)	Kootapalo (%)	Veličina čestica (mm)		
Sjemenke grožđa	313	16 18 20	---	10,2	---	0,75	Grožđano ulje	**Passos i sur. (2008)**
Sjemenke grožđa	310 353	25	7	---	---	1,125 0,638 0,363	Ulje bogato *α*-tokoferolom	**Bravi i sur. (2007)**
Sjemenke grožđa	313 323 333	20 30 40	1,5	32,33	---	0,380	Grožđano ulje	**Jokić i sur. (2016)**
Komina grožđa	308 328	10 40	3	0,8	Etanol (5)	0,165 0,261 0,319	Resveratrol	**Casas i sur. (2010)**
Komina grožđa	318	10 15 25	---	18,3	Metanol (5)	---	Polifenoli	**Louli, Ragoussis i Magoulas (2004)**
Kožica grožđa	313	15	0,25	2	Etanol (7.5)	---	Resveratrol	**Marti i sur. (2001)**
Trop bazge	313	21	1,6	---	CO_2 (0-90) Etanol (0.5-100) H_2O (0–95)	---	Antocijanini	**Seabra i sur. (2010)**
Otpad od prerade soka marelice	316–350	13,3–47,3	1,5	1	Etanol (2–28)	0,07-0,6	*β*- karoten	**Sanal i sur. (2005)**
Koštice marelice	313-343	30-60	---	1-5	Etanol (0-3)	0,425 -1,5	Ulje koštica marelice	**Özkal, Yener i Bayındırlı (2005)**
Koštica breskve	303 313 323	10 20 30	2,5	8,3	Etanol (2, 5)	0,25-0,35	Ulje koštica breskve	**Mezzomo i sur. (2010)**
Kožica rajčice	313-373	20-40	1,5	1-2	---	---	Likopen	**Chun i sur. (2009)**
Kožica rajčice	313 343	25 45	0,17-0,33	6,38	Etanol (5,15)	0,5–1	Likopen	**Kassama, Shi i Mittal (2008)**
Kožica i sjemenke rajčice	313 333 353	30 38 46	---	---	---	0,3 0,4 0,6	Karotenoidi Tokoferoli Sitosteroli	**Vagi i sur. (2007)**
Trop jabuke i kruške	313–333	20–60	0,17– 0,67	2	Etanol (14–20)	0,638	Polifenoli	**Adil i sur. (2007)**
Koštice višnje	313-333	18-22	---	---	---	1,25-2,25	Ulje iz koštica višnje	**Bernardo-Gil i sur. (2001)**
Kora narandže	293 - 323	8-28	---	8,3 – 58,3	---	0,1- 10	Eterično ulje	**Mira i sur. (1999)**
Kora narandže	313	10	1	29,3	---	0,324	Eterično ulje	**Jerković i sur. (2015)**
Kora citrusa	333	9,5	0,75	---	Etanol (15)	---	Naringin	**Giannuzzo i sur. (2003)**
Komina masline	323	35	3	33	Etanol (10)	---	Tokoferoli	**Ibáñez i sur. (2000)**
Komina masline	313-323	10-30	2,5	1,8-2,7	Etanol (10)	0,30 – 0,55	Maslinovo ulje	**De Lucas, Rincon i Gracia (2003)**
Kakao ljuska	323 358	15-45	---	---	---	2-4	Teobromin	**Rossi (1996)**
Pogača nakon prešanja konopljinog ulja	313 323 333	20 30 40	1,5-7,5	11,7 29,1 46,7	---	---	Konopljino ulje Odmašćena pogača	**Aladić i sur. (2016)**
Nusproizvodi riže	**353**	**68**	**---**	**1,082**	**---**	**---**	**Tokokromanol Orizanol**	**Perretti i sur. (2003)**

SUVREMENE TEHNIKE EKSTRAKCIJE NA PTFOS





Primjer – sjemenke marelice



Pogača – odličan izvor proteina – enzimska hidroliza kao efikasna metoda za dobivanje visokovrijednih proteinskih hidrolizata sa poželjnim bioaktivnim svojstvima (u suradnji s Tehnološkim fakultetom Novi Sad)

Primjer – komina grožđa

Komina

Sušenje →

\+

OSTATAK

Prešanje/
Ekstrakcija →

\+

Ekstrakcija → Proantocijanidini (RESVERATROL)

POLIFENOLI U NEKIM SORTAMA:

- **Chardonay 2,52%**
- **Muskat 2,70%**
- **R. Rizling 2,15%**
- **Zweigelt 4,56%**

PRIMJENA:

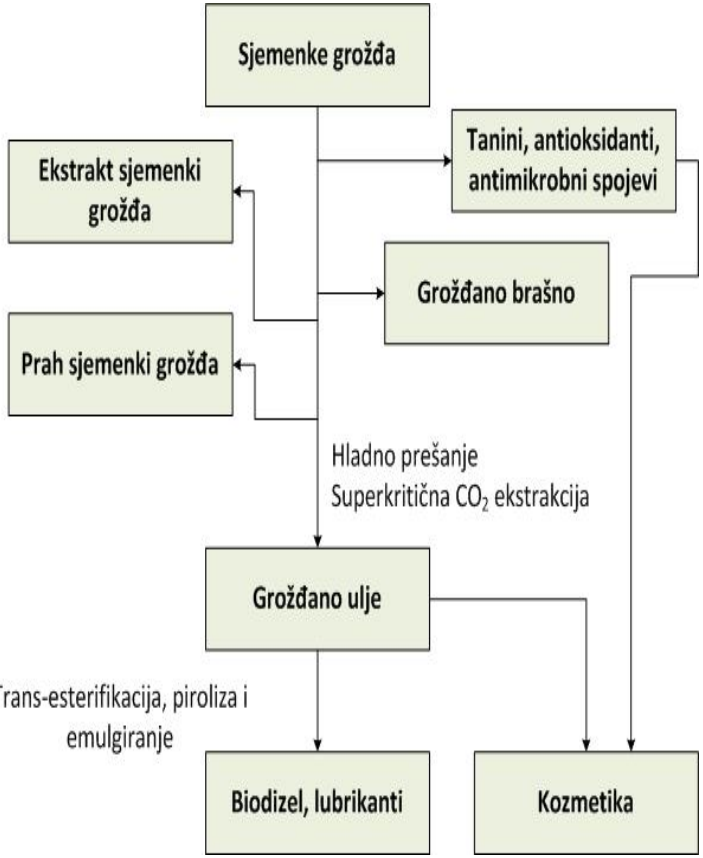
– kao koncentrat proantocijanidina (u kolaču je smanjena vlaga i ulje);

– kao grožđano brašno koje se dodaje u pekarske proizvode do 10%, pa i više;

– potencionalno velika primjena u obradi voda jer su bogat izvor lignoceluloze koja uz određenu kemijsku modifikaciju mogu poprimiti karakteristike anionskih izmjnjivača

–potencijalni „low cost" adsorbens za uklanjanje nitrata iz voda i otpadnih voda

Primjer – sjemenke grožđa



Primjena?

Popis mogućih proizvoda od tropa nakon otakanja mošta

1. **Hladno prešano ulje grožđanih koštica**
   Hladno prešano ulje u pakovanju 0,1 i 0,25 l. Nefiltrirano. Primjena kao salatno ulje, ali i za kuhanje i pečenje
   Intenzivno se koristi u kozmetici, a posebno u wellness programima odnosno aromaterapijama.

2. **Brašno od grožđanih koštica**
   Ostatak od prešanja se melje u brašno koje je izrazito bogato antioksidansima. Dodaje se 5-7% pšeničnom brašnu, ili se rade specijalan dijetna brašna

3. **Tjestenina od grožđanih koštica**
   Sastoji se od durum pšenice i 5-7% grožđanog brašna

4. **Krekeri od brašna grožđanih koštica**
   Sastoje se od integralnog brašna i grožđanog brašna

5. **Snack prutić od grožđanih koštica**
   Sadrži med, smeđi šećer, žitarice, konc. Sok jabuke, grožđano brašno..

6. **Kapsule s grožđanim košticama**
   Sadrže 600 mg grožđanog brašna i najveći su izvor procijanidina, katehina i epikatehina

7. **Gotova integralno brašno**
   Sastoji se iz integralnih sastojaka ; pšenica, raž, sjeme suncokreta, soja, suhi kvasac, grožđano brašno…..

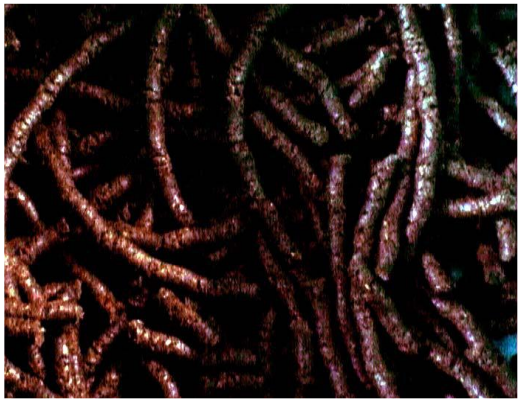
8. **Dodatak stočnoj hrani**

PREŠANJE ULJA

Klipna preša – Eigenbau Fimbinger

„Zaostali“ kolač od prešanja sjemenki pomoću klipne preše

Pužna preša KOMET CA 59 G



Kolač koji zaostaje nakon prešanja pomoću pužne preše

Primjer – ulje iz sjemenki grožđa

Sastav sjemenki grožđa:

- voda 25 - 45 %
- ugljikohidrati 34 - 36 %
- organske kiseline 2 - 7 %
- ulje 5 - 20 % (varira između bijelog i crvenog grožđa)
- polifenoli do 6,5 %
- minerali 2 - 4 %.

- ❑ prirodni izvor bioaktivnih fenolnih tvari
  - ✓ pozitivni farmakološki i nutritivni učinci
  - ✓ primjena u tehnološkim postupcima
- ❑ dodatna valorizacija grožđa kao sirovine

Sadržaj masnih kiselina u grožđanom ulju

Zasićene masne kiseline	Palmitinska (C 16:0)	4 – 6 %
	Stearinska (C18:0)	2 - 4 %
Nezasićene masne kiseline	Palmitooleinska (C16:1)	2 - 6 %
	Oleinska (C18:1)	13 - 31 %
	Linolna (C18:2)	50 - 76 %

Primjer – sjemenke grožđa

Graševina

Cabernet sauvignon

Zweigelt

Seed preparation

- Seeds screened from pomace
- Seeds screened from pomace and washed
- Seeds screened from pomace after drying

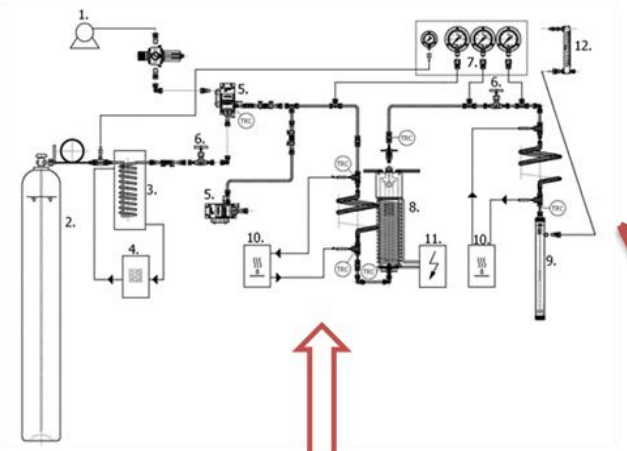
Grape seeds

Drying

- Natural drying
- Chamber drying

Grounded grape seeds

Supercritical CO2 extraction



Deffated meal

Grape seed oil

Primarna prerada

Zaprimanje svježe sirovine
Rasipanje grumena
Odvajanje od opne
Kalibriranje koštice

Prerada

Izvor http://www.oekotec.ibg-monforts.de/

Prešanje
- Klipna preša
- Kontinuirana preša

Filtriranje
- Sedimentacija
- Centrifuga
- Pločasti filteri

Prerada

Izvor http://www.oekotec.ibg-monforts.de/

Prešanje
- Klipna preša
- Kontinuirana preša

Filtriranje
- Sedimentacija
- Centrifuga
- Pločasti filteri

TRŽIŠNE CIJENE

- Ulje sjemenki grožđa 300 – 1000 kn po litri (rinfuza – pakiranje 0,1l)
- Ekstrakt sjemenke grožđa 110 kn za 50g (kapsule)
- Ekstrakt kožice grožđa oko 170 kn za 300g (566 kn/kg)
- Peleti 1,20 kn/kg

Kamilica (*Matricaria chamomilla*)

Uzorci kamilice dobiveni tijekom različitih faza prerade (tvrtka Matricia d.o.o., Široko polje):

a) b) c) d)

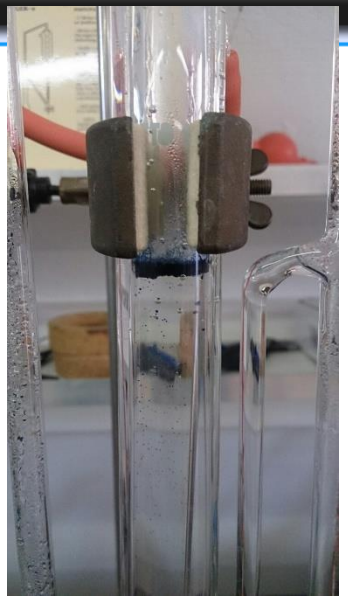
a) nedorađeni cvijet kamilice I. klase
b) dorađeni cvijet kamilice I. klase
c) otpad od dorade
d) pulvis

- Proizvodnja ekstrakata primjenom SC-CO_2 i drugih tehnika ekstrakcije (tlačno-tekućinska, Soxhlet, hidrodestilacija...)
- Određivanje antioksidacijske aktivnosti & sadržaja umbeliferona primjenom HPLC.

- Značaj istraživanja - mogućnost korištenja otpada iz procesa prerade kamilice, kao i dobivanja krajnjeg proizvoda pomoću SC-CO_2 ekstrakcije koji je sasvim prirodan, bez rezidua organskih otapala sa potencijalnom primjenom u kozmetičkoj industriji.

Kamilica (*Matricaria chamomilla*) – proizvodnja eteričnih ulja

lab



pilot

FUTURE RESEARCH

hrzz
Croatian Science Foundation

ByProExtract

***NEW Installation Research Projects*: „Application of innovative techniques of the extraction of bioactive components from by-products of plant origin”** *(2018-2023)*

Principal Investigator: Stela Jokić

*(Budget: **1.607.708,72 HRK**)*

PTF OS

Hrvatski veterinarski institut
1933
Zagreb

Sveučilište Josipa Jurja Strossmayera u Osijeku
Medicinski fakultet Osijek

UNIVERZITET U NOVOM SADU
TEHNOLOŠKI FAKULTET NOVI SAD

ByProExtract

Kakao ljuska

Kore citrusa

Otpad iz proizvodnje duhana

a) Duhanska prašina

b) Rebro lista duhana

c) Refabrikat

Primjer-kore citrusa

No.	Compound	RI	Area percentages (%) A	B	C	D
1	trans-Hex-2-enal	< 900	0.1	0.1	0.1	0.1
2	Heptanal	< 900	0.1	0.1	0.1	0.1
3	α-Pinene	941	2.0	1.3	1.6	0.2
4	Sabinene	982	10.0	5.1	9.8	0.5
5	β-Myrcene	994	-	3.7	-	0.7
6	Octanal	1007	-	-	-	0.8
7	Limonene	1036	54.3	52.1	48.2	48.1
8	trans-Sabinene hydrate	1069	-	0.5	0.2	-
9	α-Terpinolene	1094	0.1	0.1	0.1	-
10	Linalool	1107	5.9	5.3	3.0	3.5
11	p-Cymene	1032	-	-	-	0.2
12	trans-p-Mentha-2,8-dien-1-ol*	1138	0.1	1.5	0.3	4.8
13	trans-Limonene oxide**	1155	0.1	-	-	-
14	Citronellal	1166	0.1	0.2	0.1	-
15	Terpinen-4-ol	1185	0.1	0.4	0.2	0.9
16	α-Terpineol	1198	0.7	2.4	0.8	2.3
17	Decanal	1211	0.8	1.8	1.0	1.7
18	trans-Carveol	1218	0.1	0.8	0.2	3.3
19	cis-Carveol	1231	-	-	-	1.7
20	(Z)-Citral	1252	0.5	1.8	0.6	-
21	Carvone**	1253	-	-	-	3.2
22	Geraniol	1273	-	0.2	-	-
23	Linalyl acetate	1254	5.0		1.5	
24	p-Mentha-1,8-dien-3-one (Isopiperitone)**	1279	-	-	-	1.6
25	(E)-citral	1282	0.7	1.9	0.7	-
26	p-Mentha-1,8(10)-dien-9-ol*	1305	0.2	0.8	0.2	-
27	1H-Indole	1301	0.3	-	0.3	-
28	(E,E)-Deca-2,4-dienal	1325	0.1	0.1	0.1	0.3
29	δ-Elemene	1344	0.1	-	0.1	-
30	Neryl acetate	1366	0.1	0.2	0.1	-
31	α-Copaene	1383	t	0.6	0.2	0.6
32	Geranyl acetate	1385	0.4	0.1	0.2	
33	Dodecanal	1413		0.6	0.3	0.5
34	Decyl acetate	1415	0.3			
35	trans-Caryophyllene	1419	0.3	0.4	0.3	0.3
36	trans-β-Farnesene	1464	0.2	0.7	0.4	0.6
37	Dodec-2-enal*	1472	0.1	-	0.1	-
38	α-Amorphene	1480	-	0.1	-	0.2
39	Germacrene D	1487	0.7	0.7	0.4	
40	Valencene	1496	-	0.7	0.6	0.6
41	(E,E)-α-Farnesene	1508	0.1	0.6	0.4	0.4
42	δ-Cadinene	1530	0.1	0.8	0.3	0.2
43	Elemol	1556	-	0.1	0.1	-
44	Germacrene B	1562	0.1	-	-	0.5
45	Nerolidol	1569	0.5	0.1	0.2	0.5
46	Spathulenol	1585	-	-	-	2.1
47	Caryophyllene oxide	1589	-	0.4	0.1	-
48	Dihydro-cis-α-copaene-8-ol**	1632	-	0.2	0.1	-
49	β-Sinensal	1702	-	0.9	0.2	0.4
50	Farnesol*	1735	0.2	0.2	0.3	0.9
51	(E.E)-Farnesal	1741	-	0.2	-	-
52	α-Sinensal	1754	-	0.5	0.3	0.2
53	Nootkatone	1815	0.5	0.1	0.3	0.2
54	Hexadecanal	1820	-	0.2	0.1	0.5
55	Hexadecan-1-ol	1882	0.3	0.4	0.3	0.9
56	Methyl hexadecanoate	1937	-	0.2	0.1	0.4
57	6,7-Dimethoxycoumarin (Scoparone)	1993	0.1	0.5	0.4	0.5
58	Bergapten	2068	0.7	-	1.4	-
59	Octadecan-1-ol	2084	0.3	-	0.5	2.3
60	Osthole	2143	0.9	-	1.1	-
61	(Z)-Octadec-9-en-1-ol	2060	0.1	0.1	1.3	1.6
62	Docosane	2200	-	1.0	-	0.4
63	7-Methoxy-8-(2-formylpropyl)coumarin*	2238	0.2	-	1.1	-
64	Isogeijerin (7-methoxy-6-(3-methyl-2-oxobutyl)-2H-1-benzopyran-2-one	2347	11.2	2.0	15.3	3.0
65	Tetradecane	2400	-	1.0	-	2.0
		Total identified	98.1	99.8	95.7	93.8

The profiles of **SC-CO_2 extracts** of Citrus peels (A-D) determined by GC-FID/MS:

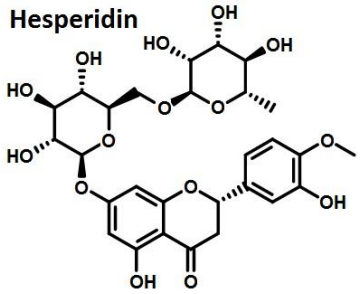
Citrus aurantium L. (**A**),
C. sinensis Osbeck cv. Washington navel (**B**),
C. sinensis cv. Tarocco (**C**)
C. sinensis cv. Doppio Sanguigno (**D**).

Primjer-kore narandža i mandarina

SFE

GC/MS

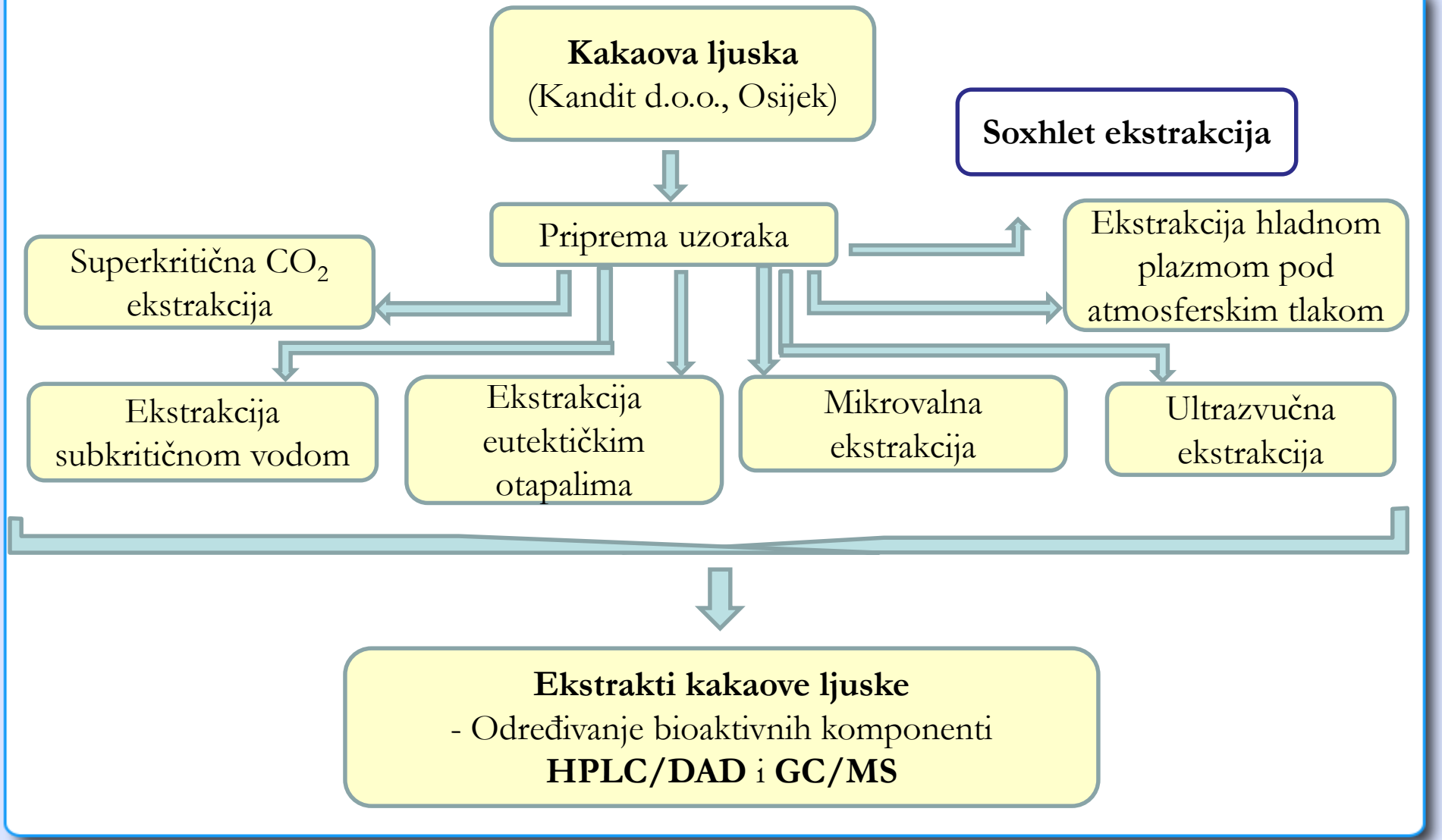
SFE



UZV

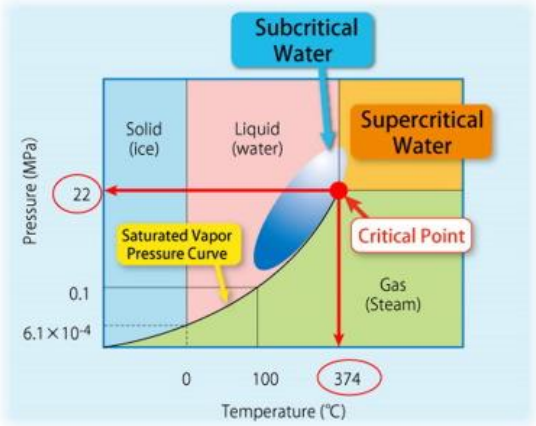
HPLC

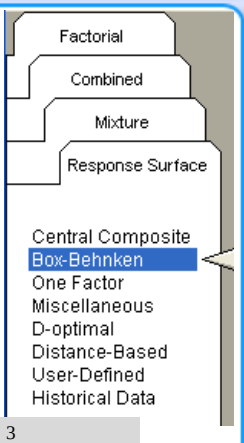
Compound	Rt	RI	Zorana		Kuno		Okica		Chahara	
			100 bar	300 bar	100 bar	300 bar	100 bar	300 bar	100 bar	300 bar
α-Thujene	4,082	932	-	-	0.1	0.1	-	-	-	-
α-Pinene	4,237	940	-	-	0.6	0.3	-	0.1	-	-
Sabinene	5,091	978	-	-	0.2	0.1	-	0.1	-	-
β-Pinene	5,191	982	0.1	-	0.4	0.3	0.1	0.1	-	-
β-Myrcene	5,478	992	0.6	0.4	2.3	1.9	0.5	1.0	0.1	0.1
Octanal	5,783	1003	-	-	0.1	0.1	0.1	0.1	-	-
Phellandrene	5,876	1007	-	-	0.1	0.1	-	-	-	-
p-Cymene	6,440	1028	1.2	1.1	0.1	0.1	0.5	0.9	0.3	0.1
Limonene	6,602	1034	37.2	35.1	66.8	66.6	35.4	52.8	11.7	3.5
trans-β-Ocymene	7,110	1051	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
γ-Terpinene	7,467	1062	3.9	4.4	8.4	8.5	5.0	6.6	1.3	1.0
cis-Sabinene hydrate	7,755	1071	0.1	0.1	0.1	0.1	0.1	0.1	-	-
α-Terpinolene	8,437	1089	0.4	0.4	0.6	0.6	0.4	0.6	0.2	0.1
Linalool	8,855	1100	3.4	4.3	1.6	1.7	3.0	2.6	4.3	2.2
Nonanal	8,891	1101	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Citronellal	10,793	1155	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Terpinen-4-ol	11,744	1179	0.2	0.3	0.1	0.1	0.2	0.2	0.3	0.2
α-Terpineol	12,286	1191	1.4	1.6	0.6	0.6	1.2	0.9	2.0	2.2
Decanal	12,864	1204	0.6	0.7	0.4	0.4	0.6	0.4	0.8	0.6
trans-Carveol	13,405	1219	-	-	-	-	0.1	-	-	-
Citronellol	13,809	1230	0.3	0.3	0.1	0.1	0.2	0.1	0.2	0.1
(Z)-Citral	14,283	1242	-	-	0.1	0.1	-	-	-	-
(E)-Citral	15,511	1271	-	-	0.1	0.1	-	-	-	-
Thymol	16,609	1295	0.2	0.4	-	-	-	0.3	-	-
Carvacrol	16,992	1304	0.7	0.9	0.1	0.1	0.1	0.1	0.4	0.6
Undecanal	17,023	1305	-	-	0.1	-	0.1	-	-	-
δ-Elemene	18,253	1337	0.5	0.5	0.2	0.2	0.5	0.3	0.8	0.6
Citronellyl acetate	18,982	1354	-	-	-	-	0.2	0.2	0.3	0.1
Neryl acetate	19,452	1365	0.4	0.4	0.1	0.1	0.2	0.2	0.4	0.4
α-Copaene	19,881	1375	1.3	1.4	0.5	0.6	1.2	0.9	1.7	1.1
Geranyl acetate	20,255	1384	0.6	0.6	0.2	0.2	0.9	0.6	1.1	1.1
β-Cubebene	20,419	1387	1.1	1.1	0.5	0.5	1.1	0.8	1.3	0.9
β-Elemene	20,518	1389	2.9	2.9	0.5	0.5	2.9	1.9	3.8	3.2
Dodecanal	21,254	1407	0.2	0.2	0.1	0.1	0.1	0.1	0.3	0.2
Limonen-10-yl acetate	21,349	1409	0.3	0.3	0.1	0.1	0.5	0.3	0.7	0.3
trans-Caryophyllene	21,572	1415	1.2	1.2	0.3	0.3	1.1	0.8	1.6	1.5
α-Guaiene	22,373	1436	0.2	-	0.1	-	0.2	0.1	0.3	0.1
α-Humulene	22,953	1450	2.1	2.0	0.5	0.5	2.4	1.4	2.8	2.6
Germacrene D	24,085	1477	5.0	4.9	1.9	1.9	5.5	3.2	7.2	7.6
Valencene	24,564	1489	0.3	0.3	0.1	0.1	0.6	0.3	0.4	0.9
Bicyclogermacrene	24,698	1492	1.1	1.1	0.3	0.3	1.6	0.9	1.9	2.8
α-Muurolene	24,873	1496	-	-	0.1	0.2	-	-	0.7	0.9
Eremophilene	25,064	1500	10.4	10.4	2.6	2.8	11.1	7.2	15.2	18.6
(E,E)-α-Farnesene	25,294	1506	7.6	7.5	3.5	3.5	8.8	5.3	12.8	15.8
δ-Cadinene	25,808	1520	1.9	1.9	0.7	0.7	1.7	1.1	2.6	3.2
Elemol	26,833	1547	0.2	0.2	-	-	0.1	0.1	0.2	0.1
Germacrene B	27,026	1552	0.9	0.9	0.3	0.3	0.9	0.5	1.4	1.7
Dodecanoic acid	27,640	1568	0.2	0.2	-	-	0.1	-	0.3	0.9
Spathulenol	27,873	1574	0.1	-	-	-	-	-	-	-
Tetradecanoic acid	34,903	1764	0.6	0.7	0.2	0.3	0.4	0.3	0.8	2.6
Hexadecanoic acid	41,697	1966	1.8	2.4	0.6	1.1	2.0	1.4	5.4	4.8
Linoleic acid	47,065	2132	0.5	0.5	0.6	1.0	2.1	0.9	4.2	11.3


Kakaova ljuska
(Kandit d.o.o., Osijek)
Soxhlet ekstrakcija
Priprema uzoraka
Superkritična CO_2 ekstrakcija
Ekstrakcija hladnom plazmom pod atmosferskim tlakom
Ekstrakcija subkritičnom vodom
Ekstrakcija eutektičkim otapalima
Mikrovalna ekstrakcija
Ultrazvučna ekstrakcija
Ekstrakti kakaove ljuske
- Određivanje bioaktivnih komponenti
HPLC/DAD i GC/MS

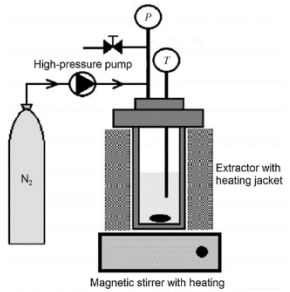
KAKAO LJUSKA

Cocoa shells – by-product of Chocolate factory Kandit (Osijek)





$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i \cdot X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} \beta_{ij} X_i X_j$$



17 experiments at:

- Temperature (120-220 °C)
- Extraction time (15-75 min)
- Solvent-solid ratio (10-30 mL/g)

HPLC

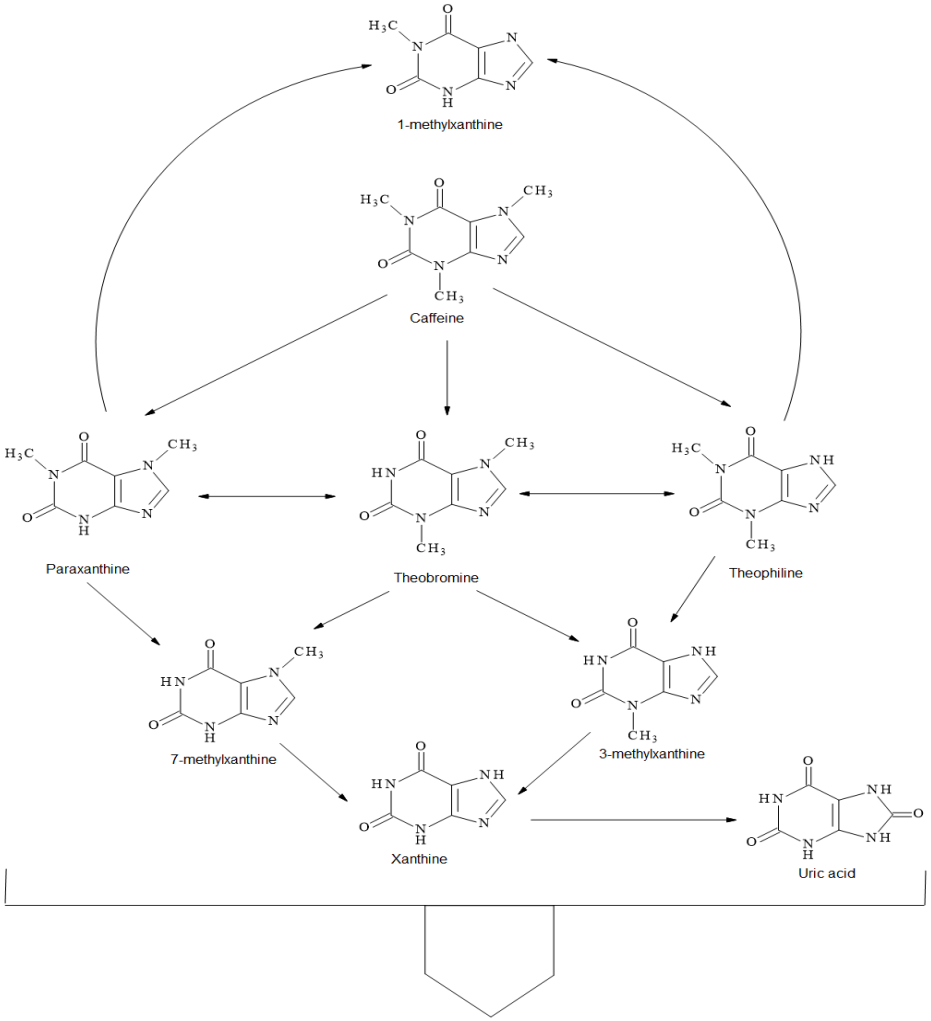
Observed characteristics:

- Theobromine, caffeine, theophylline
- Content of TP
- Gallic acid, catechin, epicatechin, chlorogenic acid
- 5-HMF
- Sugar coontent
- Antioxidant activity

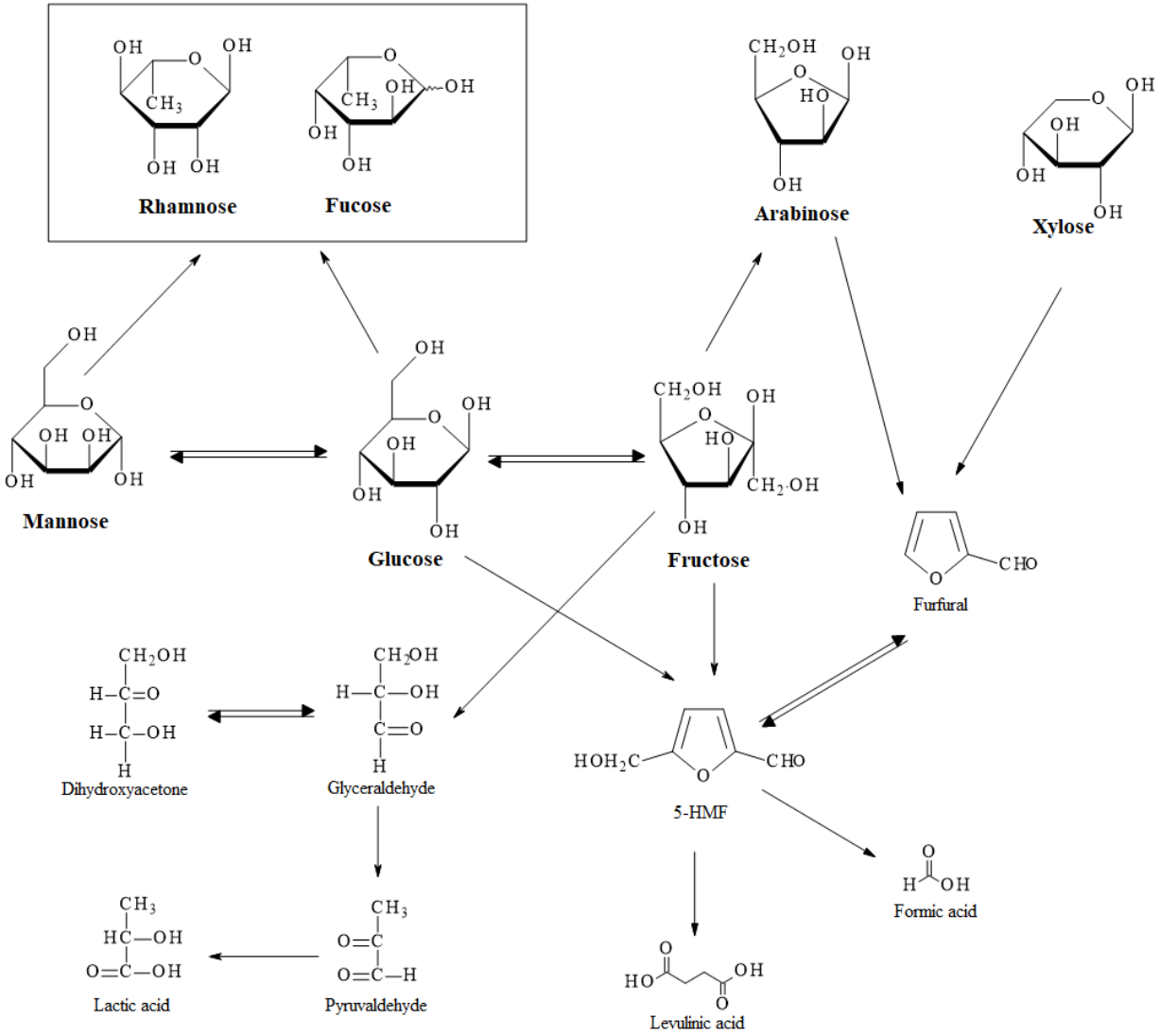
Run	Temperature (°C)	Time (min)	Solvent-solid ratio (mL/g)	Theobromine % (w/w)	Caffeine % (w/w)	Theophylline % (w/w)	Gallic acid % (w/w)	Epicatechin % (w/w)	Catechin % (w/w)	Chlorogenic acid % (w/w)	TP (mg GAE/g extract)	% DPPH scavening
1	170	45	20	4.15	0.23	traces	traces	1.13	traces	traces	95.97	62.99
2	120	75	20	2.94	0.13	-	-	0.63	traces	traces	27.26	19.20
3	170	45	20	4.77	0.23	traces	traces	0.94	traces	traces	94.18	52.06
4	170	75	30	3.45	0.24	traces	-	0.58	traces	traces	57.01	48.36
5	120	45	30	1.63	0.07	-	-	0.59	traces	traces	43.67	31.27
6	170	75	10	4.32	0.19	traces	traces	0.44	traces	traces	91.10	64.48
7	120	45	10	1.31	0.04	-	-	0.41	traces	-	98.28	63.83
8	220	45	10	3.57	0.17	0.45	-	0.23	0.37	0.01	93.41	66.33
9	120	15	20	2.12	0.10	-	-	0.66	traces	-	94.44	65.46
10	170	15	10	3.83	0.29	-	traces	1.23	traces	traces	96.49	70.51
11	170	45	20	4.26	0.21	traces	traces	0.85	traces	traces	101.35	74.47
12	170	45	20	3.30	0.20	traces	traces	0.55	traces	traces	85.72	80.60
13	170	15	30	2.95	0.25	traces	-	3.29	traces	traces	33.41	20.24
14	170	45	20	3.57	0.24	traces	traces	0.47	traces	traces	113.41	71.89
15	220	45	30	3.27	0.16	0.04	-	0.19	0.29	0.01	117.51	83.62
16	220	15	20	3.27	0.14	0.07	-	0.38	0.07	0.01	44.95	33.67
17	220	75	20	3.65	0.18	0.17	-	0.25	0.45	0.03	130.33	91.69

Run	Temperature (°C)	Time (min)	Solvent-solid ratio (mL/g)	glucose	rhamnose	arabinose	mannose	xylose	fucose	levulinic acid	lactic acid	formic acid	5-HMF	furfural
1	170	45	20	0.89	1.82	5.85	-	2.93	1.70	-	-	-	Traces	Traces
2	120	75	20	-	-	-	1.17	-	-	-	-	-	-	-
3	170	45	20	2.76	1.71	3.27	-	3.61	1.46	-	-	-	Traces	Traces
4	170	75	30	3.21	2.84	4.57	-	3.94	2.04	-	-	-	Traces	Traces
5	120	45	30	-	-	-	0.91	-	-	-	-	-	-	-
6	170	75	10	2.84	2.35	3.92	-	3.66	1.88	-	-	-	Traces	Traces
7	120	45	10	-	-	-	0.68	-	-	-	-	-	-	-
8	220	45	10	2.67	5.74	5.71	-	5.18	5.20	10.95	6.69	1.96	Traces	Traces
9	120	15	20	-	-	-	0.27	-	-	-	-	-	-	-
10	170	15	10	1.02	1.09	1.13	-	2.97	1.05	-	-	-	Traces	Traces
11	170	45	20	1.19	1.53	3.48	-	3.56	1.32	-	-	-	Traces	Traces
12	170	45	20	1.34	-	3.78	-	3.25	1.23	-	-	-	Traces	Traces
13	170	15	30	1.32	1.47	2.88	-	3.22	0.98	-	-	-	Traces	Traces
14	170	45	20	1.53	1.94	3.09	-	2.90	1.66	-	-	-	Traces	Traces
15	220	45	30	4.61	5.93	6.48	-	4.22	4.70	11.83	7.07	2.37	0.35	0.69
16	220	15	20	2.36	4.20	4.59	-	4.60	4.26	6.37	6.38	0.36	0.96	2.62
17	220	75	20	4.22	6.00	6.57	-	5.84	5.65	7.44	4.18	3.25	0.030	0.41

Proposed degradation mechanism of methylxanthines within hydrothermal degradation of cocoa shell



Proposed mechanism of sugar degradation within hydrothermal degradation of cocoa shell



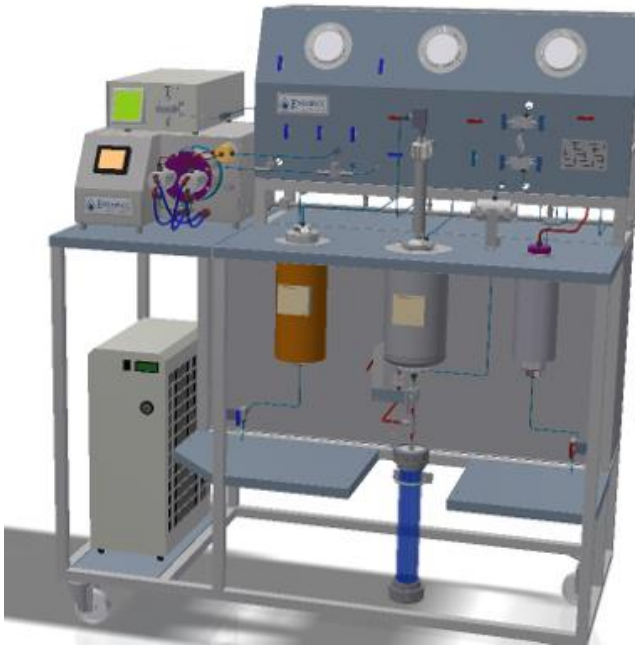
University of Maribor

Faculty of Chemistry and Chemical Engineering

FUTURE RESEARCH

Novoodobreni bilateralni projekt Hrvatska - Slovenija: Separacija aktivnih komponenta iz nusproizvoda prehrambene industrije – kakao ljuske i formulacija praškastih produkata (2018-2020)

- voditelji: Stela Jokić (HR) i Mojca Škerget (SLO)



- *Istraživački rad obuhvatit će formulaciju proizvoda u praškastom obliku visokotlačnim mikronizacijskim procesima (PGSS) pomoću superkritičnih tekućina i karakterizaciju dobivenih proizvoda*

PGSS® Particles from Gas-Saturated Solutions

ogućnosti iskorištenja
mbene industrije“

idbi stoke. Prema UROSTAT-a, reci- o 10 % tako nas- la“. Nusproizvodi e industrije sadr- udio organske tva- a jako opterećuju emeno, to su bo- aktivnih spojeva, oteina koji imaju ijal primjene u j industriji, proiz-

vodnji energije i slično.

U želji da knjiga predstavi što kvalitetniji i sveobuhvatniji pogled na problematiku, poziv za pisanje poglavlja u knjizi poslan je znanstvenicima koji se bave istraživanjima na navedenom području u Hrvatskoj i susjednim državama. Rezultat je toga monografija u kojoj 41 autor u 13 poglavlja opisuje nusproizvode s različitih aspekata: opisane su tehnike i procesi ekstrakcije bioaktivnih sastavnica, primjena (i mogućnosti primjene) nusproizvoda i/ili njihovih ekstrakata u prehrambenoj, kozmetičkoj i farmaceutskoj industriji, obradi otpadnih voda, proizvodnji biogoriva i slično. Opisani su nusproizvodi iz tehnologije voća i povrća, ulja, mlijeka, piva, etanola i drugoga. Budući da je tema vrlo aktualna, ali i široka, autori su se dogovorili da monografija doživi i nastavak što se očekuje u skoro vrijeme.

(Đurđica Ačkar)

ZAKLJUČAK

- Prerada „otpada” u visoko profitabilne krajnje proizvode (funkcionalne prehrambene proizvode; ekstrakte bogate bioaktivnim komponentama)
- Ekološki utjecaj
- Stvaranje novog branda
- Dostupnost sirovine
- Dostupnost tehnologije
- Dostupnost sufinanciranja
- Mogućnost udruživanja proizvođača kroz proizvodne „klastere”
- Ne postojanje konkurencije na domaćem tržištu

Budućnost - Iskorištenje nusproizvoda prehrambene industrije, kao izvora funkcionalnih sastojaka u svrhu obogaćivanja postojećih i razvoja novih proizvoda

11. stručni skup

FUNKCIONALNA HRANA U HRVATSKOJ

Hvala na pažnji

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Zagreb, srpanj 2018.