Nota breve

Thlaspi arvense oil: content and potential use for biodiesel production

G. Colombo Castelli
N. Ravasio*
F. Zaccheria

CNR - Istituto di Scienze e Tecnologie Molecolari
Milano, Italy

The extraction and analysis of *Thlaspi arvense* oil was carried out using laboratory methods. *Thlaspi arvense* is a plant belonging to the *Brassicaceae* family, more commonly known as Field Pennycress. The gaschromatographic analysis results show that the oil is rich in erucic acid, a characteristic shared by the *Brassicaceae*.
On the basis of the collected data, it was decided to perform chemical transformations to make the raw oil conform to a product potentially suitable as a biofuel.
Using colorimetric titration we obtained a more complete picture of the oil's properties: it is important to establish a significant mean of the analysis results to obtain the right iodine number and the percentage of free acidity.
The transesterification and separation of the product from the glycerol phase was carried out, with further analysis highlighting a satisfactory decrease in free acidity. The oil was subsequently partially hydrogenated, thus obtaining a product that complies with the parameters of biofuels law.

Olio di *Thlaspi arvense:* un'indagine della sua composizione chimica e del potenziale utilizzo per la produzione di biodiesel

L'estrazione e l'analisi dell'olio di *Thlaspi arvense* è stata effettuata utilizzando metodi di laboratorio. *Thlaspi arvense* è una pianta appartenente alla famiglia delle *Brassicacee*, più comunemente nota come Erba Storna.
I risultati dell'analisi gascromatografica mostrano che l'olio è ricco di acido erucico, una caratteristica condivisa dalla *Brassicaceae*.
Sulla base dei dati raccolti, è stato deciso di eseguire trasformazioni chimiche per rendere l'olio grezzo conforme a un prodotto potenzialmente adatto come biocarburante.
Utilizzando titolazioni colorimetriche abbiamo ottenuto un quadro più completo delle proprietà dell'olio: è importante stabilire una media significativa dei risultati delle analisi per ottenere il giusto numero di iodio e la percentuale di acidità libera.
Effettuato lo step di transesterificazione e separazione del prodotto dalla fase glicerolo, l'analisi ha riscontrato una soddisfacente diminuzione dell'acidità libera.
L'olio è stato successivamente idrogenato parzialmente, ottenendo così un prodotto conforme ai parametri di legge in materia di biocombustibili.

(*) CORRESPONDING AUTHOR:
Dr.ssa Nicoletta Ravasio
CNR, Istituto di Scienze e Tecnologie Molecolari
Via Golgi 19, Milano, Italy
Email: n.ravasio@istm.cnr.it

INTRODUCTION

The production of biodiesel is continuously increasing, with the 2008 International Grain Council report indicating that, globally, rapeseed oil was an important source of biodiesel (4.6 million tons, i. e. 48% of total world production) followed by soya oil (2.1 million ton, 22%), and palm oil (one million tons,11%), while the rest (1.8 million tons, 19%) is produced from vegetable oil and animal fat [1].
The origin of oil seeds for the production of biodiesel varies considerably in different Countries, depending on availability and climatic conditions. Thus, rapeseed and sunflower seed oil is the main feedstock in Europe, together with palm oil produced mainly in tropical Asian countries, while in United States the main source of oil is soya produced locally and in South America.
During the last few years, the rapidly increasing production capacity and demand for biodiesel were driven both by ecological and environmental considerations as well as by government obligations concerning the use of renewable energy introduced by the European Union and the United States. On a worldwide scale, these decisions are responsible for the development of prime-material biodiesels, so that the traditional sources (soya, rapeseed, and palm) can no longer satisfy the new demand. Also, high food prices and industrial use have increased the urgency to find less expensive and non-food alternative raw materials, which represent an important and current argument in favour of research and technological development.
Second generation feedstocks are mainly represented by plants with oil seeds whose characteristics make them pertinent to the production of biodiesel. These characteristics include: adaptability to local growing conditions (rain, soil type, climatic conditions); high oil content with favourable amounts of fatty acids; compatibility with existing on-site farm infrastructure; low agricultural impact (water use, fertilizers, pesticides); well-determined growing seasons; uniform rate of seed maturation; potential markets for agricultural by-products and, last but not least, the capacity to grow in marginal and abandoned agricultural land and/or a growing season other than that in which the food products in the area are normally grown.
Many vegetable species have been taken into consideration in the past, and some still are today. Some species show positive traits, but some of their characteristics mean that their diffusion is limited and, in some cases, only locally available, while others are still under technical evaluation as regards the quality of their oil. Among the species under examination are herbaceous species, in which great interest has grown in countries with temperate climates, and arboreal species, very attractive to tropical and subtropical countries, such as *Camelina sativa* [2]. Among the various species studied, the interest in *Thlaspi arvense* shows no signs to abate.

1. THLASPI ARVENSE (FIELD PENNYCRESS)

The advantages of Field Pennycress include high seed oil, adaptability to hillsides, minimum agricultural inputs (pesticides, fertilizers, water use), its potential use in a rotational cycle, and tolerance to industrial areas.
The solvent extraction is normally carried out with hexane in order to quantitatively recover the oil, in addition to that obtained by mechanical extraction [3].
The crude oil from *Thlaspi arvense* seed has interesting physical properties, such as a higher low-temperature fluidity than many other vegetable oils such as, for example, soy oil. The oil remains fluid even at low temperatures. On the basis of this result, the oil could be useful for industrial applications or to produce liquid biofuels for transport. This quality derives from the oil of *Thlaspi arvense* containing a low quantity of saturated fatty acids [3].

2. MATERIALS AND METHODS

The oil was treated according to the following experimental procedure:
- oil extraction from seeds
- oil analysis
- evaluation of the compositional values in comparison with the parameters of European Community Standards for biodiesel
- chemical treatment of the oil to make it compliant with biodiesel Standards.

2.1 EXTRACTION OF OIL FROM SEEDS

The seeds were previously ground and dried in an oven set at 100°C for at least one night.
The extraction of the oil from *Thlaspi arvense* seeds was carried out using a Soxhlet apparatus, and employing heptane as the extraction solvent.
The extraction phase lasted approximately 6 hours. After extraction and solvent removal, the oil was stored in the fridge.

2.2 ANALYSIS OF OIL

The free fatty acid content was evaluated according to UNI EN ISO 660:2009
The determination of iodine value was realised in accordance with UNI EN ISO 3961:2013
The analysis of the composition of the fatty acids was realised in accordance with UNI EN ISO 5508:1990, UNI EN ISO 12966:2011, following the transformation of the oil into the corresponding methyl esters in accordance with ISO-5509:2000.

2.3 RESULS AND DISCUSSION

It is important to know the amount of free fatty acids because of the basic transesterification reaction that involves the formation of soaps. For the purpose of this transesterification process, should the free fatty acids

Table I – Characteristics of the crude extract

	Seed weight (grams)	Weigh extracted oil (grams)	% extracted oil	free acidity percentage	Iodine number
extraction 1	89	15	16.9	1.45	116
extraction 2	90	23	25.6	1.4	119
extraction 3	90	23	25.6	1.5	116
extraction 4	90	22	24.4	1.8	117
extraction 5	89	19	21.3	2.2	113
extraction 6	90	19	21.1	2.1	116
Averages			23.6	1.7	116.2

be present in percentages exceeding the regulatory parameters, it is useful to lower the acidity of the oil with a pre-treatment. It is also preferable for the iodine value not to exceed the limit of 120, as the presence of high levels of unsaturated fatty acids makes the biofuel highly sensitive to oxidation when compared to fossil diesel. The oxidation process is responsible for the increase in viscosity as a result of condensation reactions involving the double bonds also leading to the formation of insoluble products that can clog the filters and the injection system. On the other hand, the unsaturated bonds preserve the cold properties of the fuel (pour point, fluidity). For this reason the monounsaturated methyl oleate (C18:1Δ9) has been identified as an ideal component of biodiesel [4], and it is also present in *Thlaspi arvense* seed oil.
The crude extract analyzed showed the characteristics seen in Table I, from which it is clear that the free acidity is too high [5]. It can also be noted how the Iodine value is approaching the upper limit [6].
From the gas-chromatographic profile and the relative peak areas, it can be seen that the methyl ester of linolenic acid (C18:3 Δ9Δ12Δ15) is lower than 12%, which means that its quantitative presence is within the parameters of biodiesel for motor vehicles. The gas-chromatographic values are reported in Table II (first column), where they are compared with similar date reported by Moser [3].

2.4 TREATMENT OF CRUDE OIL

It has been established that the value for free acidity is too high, and that the Iodine value is approaching the limit. Since the trienes are present in substantial quantity, it was decided to perform a partial hydrogenation reaction of the unsaturated bonds following the transesterification reaction.
KOH in methanol solution was slowly added to a two-neck flask equipped with a dropping funnel and a reflux condenser at 40°C, and constantly stirred. The amount, in moles, of methanol is thrice that of crude oil.
It does react for two hours and extracts the upper phase (methyl ester), while the lower one is constituted of glycerol, water, potassium salts and methanol.
The hydrogenation reaction was conducted under mild conditions, in order to saturate only a few double bonds, the aim being to selectively hydrogenate linolenic acid, the only triene present in large amounts.

Table II – Characteristics of the crude and treated oil

	Crude oil	Final product
Main Fatty Acid	%	%
C16:0	3.4	3.0
C18:1	13.9	20.2
C18:2	20.5	19.2
C18:3	10.5	3.5
C20:1	10.5	11.8
C20:2	1.7	-
C22:1	36.3	37.9
Other fatty acids	3.2	4.4
Iodine Value (g I_2/100 g)	116.2	97.7
Free Fatty Acid (as oleic acid %)	2%	0.4%

The year 2009 saw the proposal of a stabilization method for highly unsaturated vegetable oils that made use of a process of selective hydrogenation under mild conditions and using a copper catalyst [7]. Here the process developed by Zaccheria was used. Hydrogenation is conducted in a reactor of 50 ml of oil with 800 mg of Cu/SiO_2 - with 3% copper - at 180°C and 8.5 bar, and protracted for two hours.
The first analysis of the treated oil was repeated, including gas chromatography, the evaluation of the Iodine value, and the free acidity by the same methods previously cited.
The analysis results were then evaluated: a comparison of the analytical values was done between the treated and the raw oil. The compared values are the results of the gas-chromatographic analysis, the evaluation of the iodine value and acid-base titrations.
Table II (second column) reports the characteristics of the treated oil. As can be seen, the presence of linolenic acid has significantly decreased, from the 10.5% down to 3.5%, while the saturation efficiency on the oleic acid was almost absent. The linoleic acid was also partially hydrogenated: it decreased from 20.5% to 15.5%. It can thus be inferred that the hydrogenation conducted under the conditions already described, and with a catalyst based on Cu/SiO_2, is selective and suitable for the purpose. It should be noted that the reaction was successful after one hour, and can therefore be considered a very fast one.
Table shows the reduction of the free acidity, which went from 2.0% of the raw material to 0.4% of the final product. This reduction results from the separation of the two components in two layers: most of the

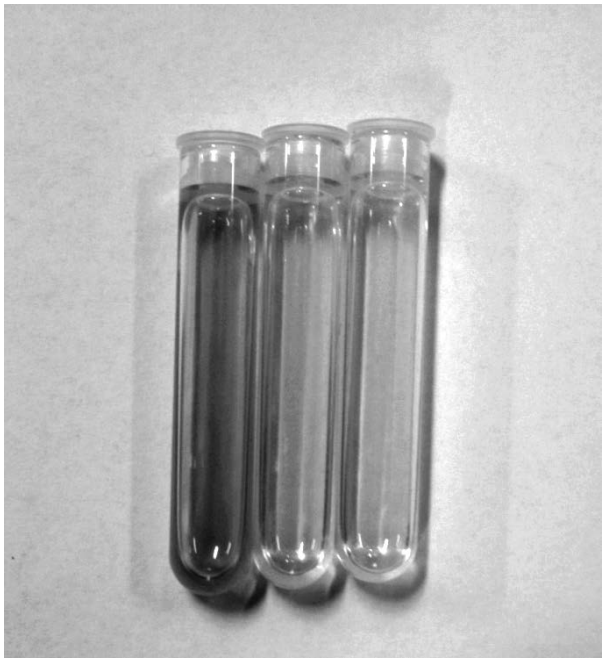

Figure 1 - Samples of dark raw oil (on the left) and more clear transesterified and hydrogenated oil.

soaps remain in the glycerol layer, with no apparent formation of soaps in the bio-oil layer. As a result of the catalytic hydrogenation reaction the Iodine value decreased from 116.2 to 97.7 (g I_2/100g)
Figure 1 depicts the biodiesel following the treatment: the crude extract is more viscous and dark, tending to an orange colour, while the transesterified is more clear and fluid, tending to yellow. The colour of the hydrogenated methyl esters is a quite pale yellow.

3. CONCLUSIONS

We can define the oil of *Thlaspi arvense* as a raw product characterized by an acceptable Iodine number value and a low presence of free fatty acids.
Thanks to its chemical composition, it can be processed into biodiesel in just one step, the one required by the transesterification process. Being the free acidity of the raw oil low, a deacidification phase is not necessary; furthermore, after the separation of the oil the small excess of acidity is confined to the glycerol layer. Another positive aspect of raw vegetable oil is that its iodine value is within the EC parameters. Additionally, the iodine value can be further reduced by means of a fast hydrogenation reaction mediated by a Cu/SiO_2 catalyst in the manner described above. In addition to being fast it is also selective in that it reduces the quantity of linolenic and linoleic acids in the final product.
Thlaspi arvense oil can therefore be considered as good, alternative raw oil for the development of biodiesels, and could be added to the list of non-traditional vegetable oils used as biodiesel. [8, 9]

REFERENCES:

[1] International Grains Council, Grain market trends in the biodiesel and Stockfeed Industries.Australian Grain *17,* 30-31 (2008)
[2] P. Pecchia, I. Brambilla, I. Galasso, S. Mapelli, Genetic and environment interaction on oil yield and quality in Camelina sativa (L.) Cranz in North Italy. 8th Euro Fed Lipid Congress, Munich, Germany, 21-24 November (2010)
[3] BR Moser, Composition and physical properties of cress (Lepidium sativum L.) and field pennycress (Thlaspi arvense L.) oils, Industrial Crops and Products *30,* 199-205 (2009)
[4] G. Knothe, 'designer' Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties, Energy and Fuels *22,* 1358-1364 (2008)
[5] UNI EN 14214 - Automotive Fuels. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods.
[6] UNI EN 14213 - Heating fuels.Fatty acid methyl esters (FAME). Requirements and test methods.
[7] F. Zaccheria, R. Psaro, N. Ravasio, Selective hydrogenation of alternative oils: as useful tool for the production of biofuels. Green Chemistry *11,* 462-465 (2009)
[8] M. Mohibbe Azam, Amtul Waris, N.M. Nahar. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. Biomass and Bioenergy Vol. *29*, Issue 4, 293-302 October (2005)
[9] Ashwani Kumar, Satyawati Sharma Potential non-edible oil resources as biodiesel feedstock: An Indian perspective, Renewable and Sustainable Energy Reviews *15* (4), 1791-1800, May (2011)

Received November 13, 2014
Accepted January 29, 2015