Recovering valuable products from Gorse (*Ulex europaeus*)

Wesley C. Miller and Ganti S. Murthy*

Biological and Ecological Engineering, Sustainable Technologies Laboratory,

Oregon State University, 116 Gilmore Hall, Corvallis, OR, 97331.

Executive Summary. Gorse *(Ulex europaeus*) is a European woody evergreen shrub which has become invasive and endemic to the Pacific coast of the United States. This paper is an investigation into potential uses of gorse. The above ground portions of gorse had 50.7% green vegetation, 11.3% flower/fragments and 38% branches/stems. Oil extractions (AOCS Method 5-04) resulted in a mean oil content of 1.33±0.01% in flowery parts of the plant, and 1.35±0.06% in the leafy portions. Extract from steam distillation (100°C) was 2.6% (w/w) of the initial dry weight. Direct distillation resulted in lower amount of volatile extracts at 60°C (2.25% w/w) as compared to 80°C (3.79% w/w). Ethanol extraction resulted in higher amount of extract (2.44%, w/w, dry basis) as compared to hexane extracted (1.22% w/w, dry basis) initial dry matter. Spectrophotometric analysis of ethanol and hexane extracts of gorse had major absorption peaks at wavelengths of 473 nm and 662 nm. Ethanol yields were estimated as 30.2±5.8 gal//ton of gorse. These yields have a potential of 30-40% increase when C5 sugar fermenting microorganisms are used in addition to yeast that can consume only C6 sugars.

Keywords. Gorse, invasive, weed, products, value-added.

* PRINCIPAL INVESTIGATOR

G. S. Murthy, Assistant Professor,

Biological and Ecological Engineering, Oregon State University

Phone: 541-737-6291 Fax: 541-737-2082 E-Mail: murthy@engr.orst.edu

Web: http://bee.oregonstate.edu/Faculty/Murthy/Murthy.htm

Introduction

With the increased movement of goods and people throughout the world, the problems caused by invasive species have become far more common. One such species is gorse (Ulex europaeus), an invasive shrub endemic to the Pacific coast of the United States (Fig. 1). The plant is a one to three meter tall perennial legume, characterized by golden yellow flowers and green thorny leaves. It is a beautiful early blooming brilliant yellow floral shrub in landscapes. Gorse is not shade tolerant, thus it will not compete in forests and other areas with full vegetative cover. When allowed to spread uncontrolled, gorse crowds out smaller plants such as pasture crops and tree seedlings for reforestation. Due to prolific seed production and spiny nature, it is difficult to control its spread in infested areas, where it invades woodlands, fields, golf courses and other open areas.

Figure 1. Gorse (*(Ulex europaeus)* plant

The bushy and aromatic nature of gorse also increases the risk of forest fires in the infested lands. Forest fire on gorse infested lands in 1936 caused extensive damage in Bandon, Oregon including loss of human life (King County Noxious Weed Control, 2008). Due to its prolific seed production and spiny growth, removal of Gorse from infested lands is both expensive and time-consuming. Analysis of gorse plant shows that it contains 13.6% crude protein, 1.9% ether extract (fat), 46.3% nitrogen extract, 34.7% fiber, 3.5% ash and 0.3% silica an a dry basis (Jobson and Thomas, 1964).

In other areas, gorse is being utilized for perfumes, soap, cosmetics and animal feed (Grieve et al, 1931; Tree Gallery, 2008). There are a number of valuable components, including oils, isoprene (Boissard et al 2007), isoflavones (Russell et al, 1990) and cellulose (Dien et al, 2006) which are potential feedstocks for different industries. Gorse is used to produce perfume and bath oil on a limited scale from locally available gorse on Caldey Island, Wales, UK (Caldey Island Products, 2008; Tree Gallery, 2008). Ashes from gorse, rich in potassium salts, are used with vegetable oils or clay to form balls of soap (Fern, 2008). The ash, being strongly alkaline will esterify the oil to produce the surfactant and unburned gorse extracts can be used to add fragrance to the product. Additionally, gorse flowers are also used for dyeing fabrics a golden yellow color (Fern, 2008) (Grae, 1974). Insecticidal properties of novel isoflavones in gorse roots have also been investigated (Russell, 1990). In the field of low impact agriculture gorse can provide a barrier and food source for animals (Tolera et al, 1997). Gorse can also be used as a non food feedstock for producing ethanol. Finding economical ways to use gorse has the potential to offset the cost (King County Noxious Weed Control Program, 2007) of removal from agricultural, forest and recreation lands. High value products such as natural dyes, soap and fragrances are currently being produced from Gorse in other areas of the world (Fern, 2008; Caldey Island Products, 2007; the-tree.org, 1984). Overall objective of this study is to investigate production of high value bioproducts and fuels from Gorse found in the Pacific Northwest of the United States. Specific objectives of this study were to:

- Characterize the distribution and variation of natural oil and pigment contents in different components of gorse (flowers, seeds and stems) during different times of year.
- Determine potential yields and uses for the extracted pigments and aromatic compounds.
- Determine potential for cellulosic ethanol from the remaining material.

Materials and Methods

Monthly samples of Gorse were collected from Bandon, Coos County, Oregon. Samples were air dried. Samples were ground in analytical mill (Tekmar A-10, Tekmar Company, Cincinnati, Ohio). Moisture content of the samples was determined using two stage convection oven method (AACC, 2005). Particle size analysis of the ground material was done with Sonic Sifter (Allen-Bradley, Milwaukee, WI) with ASTM standard sieves.

Oil Analyses

Oil content of the leaf, stalk, and flower portions of the gorse was estimated using a petroleum ether extraction process (AOCS Method 5-04). Tests have been done to determine the distribution of oils in different parts of Gorse plant. Samples (2 g) were extracted with petroleum ether in an Ankom XT10

Extraction System (Ankom Technology, Macedon, New York) (Fig. 2). Oil contents were calculated from weight loss over the extraction. Extraction was performed on 7 to 10 samples (maximum 2g size) at a time with 350ml of petroleum ether for 40min. at 90°C.

Figure 2. Mr. Wes Miller (Graduate Student) using Ankom Oil Analyzer purchased from the project funds.

Hexane and Ethanol Extraction

Samples (30.00 g) of the leafy portion and seeds were extracted in 250ml Erlenmeyer flasks with hexane (150.0g) at 30°C for 120 min in water bath. After extraction, the supernatant was decanted and filtered with a Buchner filter funnel under vacuum (0.25 atm). Subsequently, solvent was evaporated in two stages (30°C and 75°C) Moisture contents of extracted solute were determined using two stage convection oven method (AACC, 2000). Samples (leafy portion and stems) were also extracted with ethanol using the same procedure as the hexane extraction.

Steam Distillation

A vertical glass steam extraction column 0.41m long and 0.048m inside diameter was constructed (Fig. 3). It was then filled to 90% of capacity with gorse leaf/small stem material. Sample was subjected to upward steam flow for one hour from 500ml Erlenmeyer flask on hot plate (Corning PC-35, Corning Glass Company, Corning, New York) feeding steam from de-ionized water via 6.35 mm copper tube to the bottom of extraction column. Extract vapor was condensed in a 0.2m long counterflow Liebig condenser with 6.35 mm copper condensing tube enclosed in a PVC water jacket cooled with flowing tap

water to cool the condensate below 60°C. Moisture contents of steam extracted sample and original raw material were measured. Weight loss of sample was determined.

Direct Distillation

A gorse sample (23.98g) in a 250 ml Erlenmeyer flask with rubber stopper and 3.175 mm outside diameter copper distillate line was heated in a temperature controlled water bath. The vapors were condensed in a 25 ml Erlenmeyer flask immersed in a water bath maintained at 5°C. The hot bath (starting 20°C) was operated at 60°C for 24 h, followed by 80°C for 2 h. The distillate was weighed after the 60 and 80°C heating periods.

Spectrophotometry

Ethanol and hexane extraction solutions were analyzed for absorbance in spectrophotometer (UV1700, Shimadzu Corporation, Kyoto, Japan) from wavelengths from 400 nm to 800 nm. Standard cuvette with a path length of 1 cm was used for all readings. Three replicates of the absorbance readings were obtained for all samples. The main absorption peaks were determined.

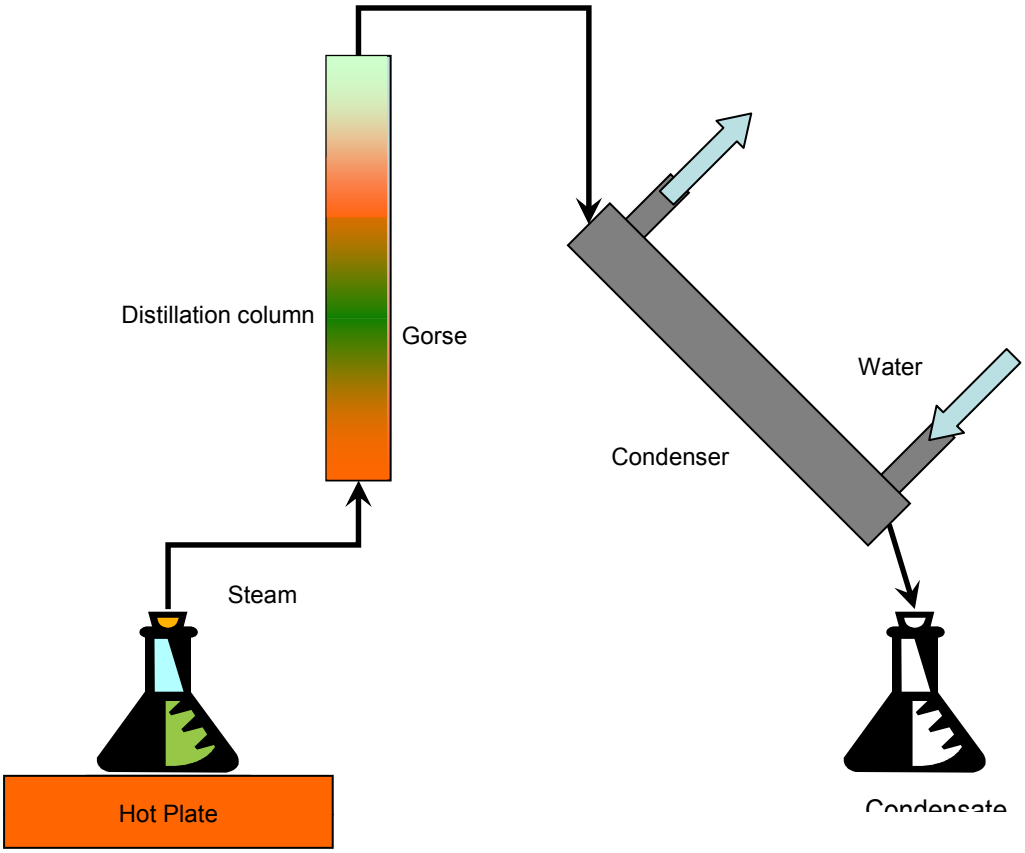

Figure 3. Steam distillation apparatus.

Ethanol Production

Pretreatment

Dilute acid pretreatment process reported by Esteghlalian et al. (1997) will be adopted for the second (duplicate) set of samples. Cleaned gorse sample were treated at 180°C and 0.75 % (w/w) dilute sulfuric acid with a 20 min residence time. The samples will be water washed and the pH adjusted before further processing.

Simultaneous saccharification and fermentation (SSF)

The hydrolysate from the pretreatment processe was fermented using SSF process recommended by NREL. Commercially available cellulose, Accelerase (Genencor, Palo Alto, CA) was used for hydrolysis. Simultaneously, fermentation was conducted by inoculating active dry yeast (*Saccharomyces cerevisae)*. The medium was be supplemented with urea to provide 300 ppm of nitrogen. The SSF process was conducted for 96 hr at a temperature of 30°C in a constant temperature waterbath. The SSF process was monitored by withdrawing samples of fermentation broth at 0, 24, and 96 hr and measuring

sugars (glucose, fructose, maltose and maltotriose), organic acids (lactic acid, acetic acid, and succinic acid) and alcohols (ethanol, glycerol and methanol) using an HPLC method. Ethanol yield potential for different treatments was calculated.

Results and Discussion

The green leafy portions constitute 62% of the air-dry weight of the gorse plant. Inspection of these fractions indicated presence of essential oils and pigments, while the remaining above ground portions were primarily brown woody fibrous material. Results of the particle size analysis of the milled gorse indicate that more than 35% of the ground material was of size 425 µm (Fig.4). In combination the 425 µm and 250 µm sieves retained more than 65% of the material, with the other distribution peak being much smaller, 17.2%, retained as fines which passed through the 149 µm (100 mesh) sieve. More than 82% of the particles were larger than 170 µm (80 mesh). Fines, defined as the material retained on the pan was 13 % of the total material.

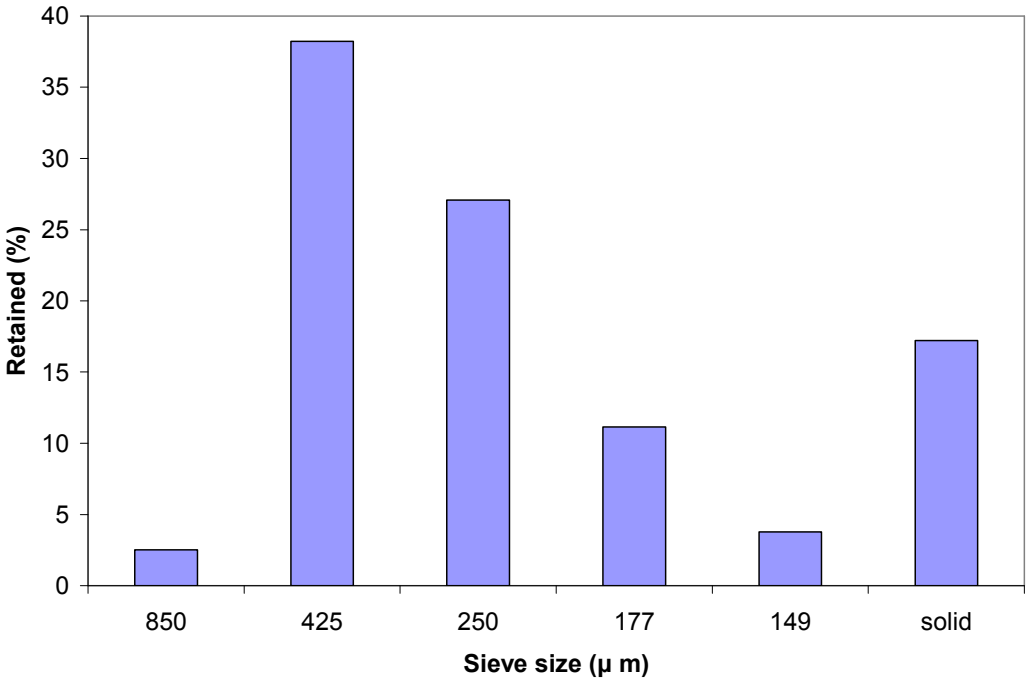

Figure 4. Particle size distribution of milled gorse.

Oil extractions with petroleum ether indicated an oil content of 1.33±0.01% (dry basis, db) in flower portion, 11.3% of total plant weight. Oil content was 1.35±0.06% (db) in the leaf portions, which accounted for 50.7% of total plant weight. Average oil content of gorse was 2.02±0.37%(db) (Fig. 5) for samples collected over eight months. In the present study, samples were collected in for 8 months during

2008. Therefore low oil contents observed could also be attributed to seasonal variations. Analysis of gorse harvested during the other part of the year could show higher oil levels.

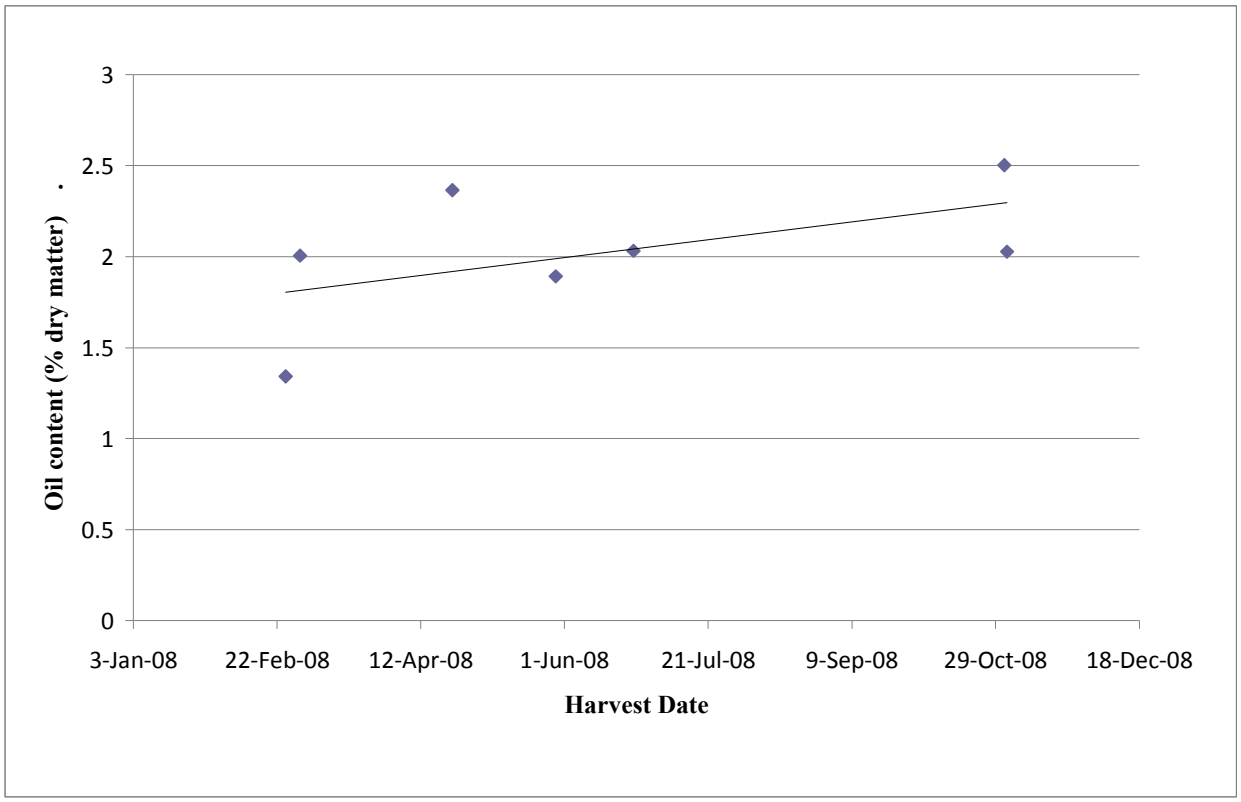

Figure 5. Gorse oil content

In the direct distillation, performed to recover volatile essential oils, a total of 3.79% (db) was condensed (Table 2). Additionally, 0.46% (db) was lost through volatiles which did not condense in the condenser. Ethanol extracted 2.44% (db) of leaf portion as dry extracted solutes, which indicates the presence of higher levels of ethanol soluble components than ether solubles. The extract also had pleasant aroma and a deep dark green color which could be used to produce dyes and other organic colorants. The hexane extraction resulted in 1.22% dry extracted solutes, a level similar to the oil extraction results. The hexane soluble material was a pale straw yellow and had less aromatic essence than the ethanol extract.

Table 2. Direct distillation of gorse.

Temperature (˚C)	Extract (%)	Cumulative (%)
20	0	0
60	2.25	2.25
80	1.54	3.79

Steam distillation extracted 2.60% of the dry weight of the sample. Condensate from steam distillation at atmospheric pressure did not exhibit a separate oil layer, indicating that the extracts from gorse will dissolve or disperse in water. In addition, the aromatic essence of the material was changed by the process from pleasant to an unpleasant "burnt" type of odor. Hence, the essential material in gorse is thermally degraded during steam extraction process. In order to prevent the degradation of the material during steam extraction, gorse was extracted using hexane (Fig. 6) and ethanol. Hexane extracted material had a more pleasant essence than the steam extracts which is attributed to doing the extractions at 30°C rather than having the material subjected to the 100°C of the steam extraction process. Ethanol extract also contained chlorophyll and had an intense green color. To quantify the color of extracts, spectorphotometric analysis of ethanol and hexane extracts was conducted.

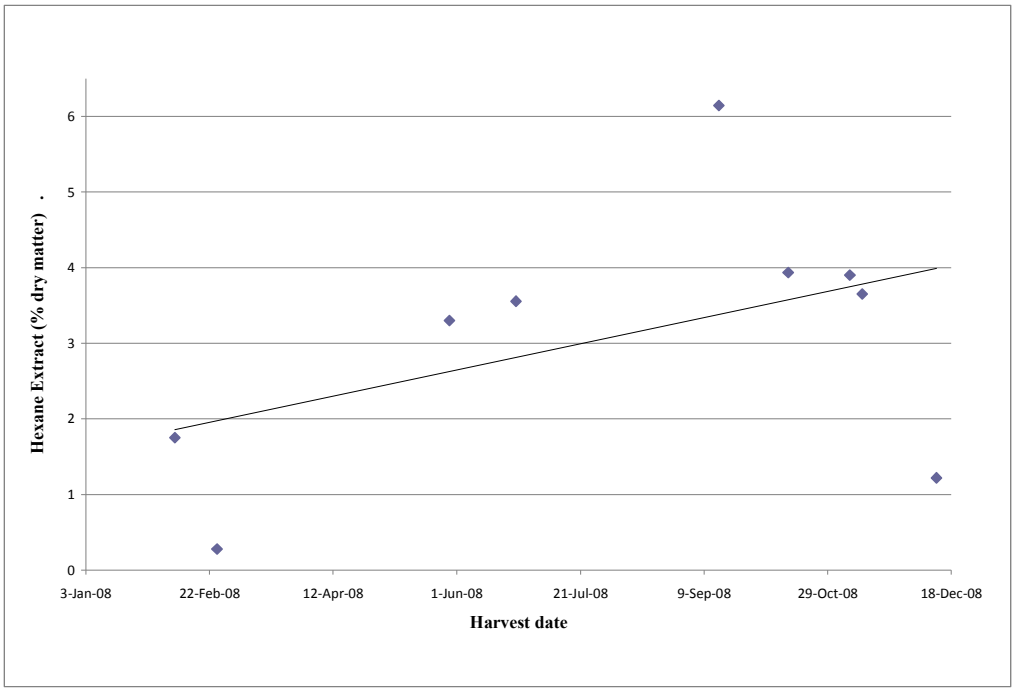

Figure 6. Hexane extraction of gorse

Spectrophotometric analysis of ethanol and hexane extracts of gorse had similar major absorption peaks at wavelengths in the areas of 473 nm and 662 nm (Table 3). Additionally, flower fraction also had peak at 618 nm (reddish orange). These absorption wavelengths indicate the presence of high levels of chlorophyll (green) in gorse. A green compound would have absorption peaks in the red (~600-750nm) and blue (400-495 nm) bands of visible spectrum with low values in yellow (570-590 nm) and green (495-570 nm) regions. We are presently evaluating the green pigment extracted (which mostly contains chlorophyll) with ethanol for dyeing applications.

Table 3. Gorse component extract absorbance values

Hexane/Leaf	470 nm/1.824A	612 nm/0.244A	666 nm/0.391A	748 nm/0.211A
Ethanol/Leaf	473 nm/3.733A	536 nm/1.294A	654 nm/3.336A	
Ethanol/Flower	475 nm/3.531A	537 nm/1.043A	618 nm/2.114A	662 nm/3.135A

Gorse was pretreated with dilute sulfuric acid to facilitate further enzymatic hydrolysis (break down of cellulose into fermentable sugars using enzymes). Pretreated gorse was hydrolyzed and simultaneously fermented by adding cellulases and yeast. Simultaneous saccharification and fermentation (SSF) process was monitored the weight loss data indicates that about 18% of the dry matter is lost during first 96 hr of fermentation. Ethanol yields were estimated as 30.2±5.8 gal//ton of gorse. These yields have a potential of 30-40% increase when C5 sugar fermenting microorganisms are used in addition to yeast that can consume only C6 sugars. More detailed characterization and experiments are being performed on gorse samples.

Table 4. Weight loss and estimated ethanol yields from gorse.

Sample	Weight loss (% dry matter)			Estimated Ethanol Conc.	Estimated ethanol yield (gal/ton)
SSF time (hr)	0	24	96		
Rep 1	100	11.40	20.60	4.26	35.1
Rep 2	100	7.20	19.60	4.14	33.4
Rep 3	100	4.20	13.00	2.94	22.2
Average	100	7.60	17.73	3.78	30.2
Std Dev.		2.95	3.37	0.60	5.8

Conclusion

There are a number of possible uses for gorse in Oregon. The above ground portions of gorse had 50.7% green vegetation, 11.3% flower/fragments and 38% branches/stems Oil extractions (AOCS Method 5-04) resulted in a mean oil content of 1.33±0.01% in flowery parts of the plant, and 1.35±0.06% in the leafy portions. Extract from steam distillation (100°C) was 2.6% (w/w) of the initial dry weight. Direct distillation resulted in lower amount of volatile extracts at 60°C (2.25% w/w) as compared to 80°C (3.79% w/w). Ethanol extraction resulted in higher amount of extract (2.44%, w/w, dry basis) as compared to hexane extracted (1.22% w/w, dry basis) initial dry matter. Spectrophotometric analysis showed the highest peaks at wavelengths corresponding to red and blue light being absorbed. This causes more of the green and yellow colors to come from the material. The high light absorption levels at visible wavelengths show high levels of colored components, with the potential for dye materials. Gorse can be

used to produce ethanol at estimated yields of 30gal/ton. Gorse is a valuable resource for production of many valuable products such as oils and dyes.

Deliverables, Timelines and Budget

Progress on deliverables: *The duration of the project is 14 months. We are on schedule to meet all objectives and deliverables. Presently no modification to project objectives/deliverables is being sought.*

Deliverables from this research:

1. Distribution of oil and pigments in different parts of gorse and their variation during one year. (we have determined the variation in oil content for 8 months)
2. Optimum time to harvest Gorse for oils and pigments (this can be determined once we complete the study).
3. Ethanol production potential from Gorse (it is estimated that 30.2±5.8 gal//ton ethanol can be produced).
4. Two reports (Mid project and Final project report) will be provided containing analysis of data collected till date. (this document is the mid project report)

A total of $30,000 is requested for the project. Estimated expenses are:

Undergraduate/Graduate Student Wages (Mr. Wes Miller is working on this project and part of his GRA is being covered using these funds)	$10,000 for undergraduate/graduate help
Services and Supplies (leveraged from another grant from GRF)	$4000 for laboratory supplies and chemicals
Equipment (Purchased)	$14,975 for purchasing lipid (oil) analyzer. Model: Ankom XT15. http://www.ankom.com
Travel	$1025 for travel
Total	$30,000

References

Boissard C., X. L. Cao, C. Y. Juan, C. N. Hewitt, M. Gallagher. 2007. Seasonal variations in V0C emission rates from gorse. *Atmospheric Environment* 35:917-927.

Caldey Island Products. 2008. www.caldey-island.co.uk (Accessed 1March2008).

California invasive plant council. 2007 Publication 2006-2. February 2007.

Dien, B. S., H. G. Jung, K. P. Vogel, M. D. Casler, J. F. S. Lamb, L. Iten, R. B.Mitchell, and G. Sarath. 2006. Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. *Biomass and Bioenergy*. 30(10):880-891.

Fern, K. 2008. Notes from observations. Plants for a Future. www.pfaf.org/database/plants.php?Ulex+europaeus. Accessed 1April 2008.

King County Noxious Weed Control Program. 2008. Gorse. http://dnr.metroke.gov.wlr/lands/weeds/gorse.htm Accessed 1 March 2008.

Grae I. 1974. Nature's Colors-Dyes from Plants. MacMillan Publishing Co. New York 67-70

Lesch, A. 1970. Vegetable Dyeing. Watson-Guptil Publications, pg 13.

Jobson H. T., B. Thomas. 1964. The composition of gorse (*Ulex euraopaeus*). *J. the Sci. of Food and Agric.* 15:652-656

Making natural dyes from plants. 2008. pioneerthinking.com. Accessed 1March2008.

Mcgrath J W. 1977. Dyes from Lichens and Plants. Van Norstrand Reinhold.

Russell, G. B., H. M. Sirat, and O. R. W. Sutherland. 1990. Isoflavones from root bark of gorse. *Phytochemistry* 29; 4 1287-1291.

The-tree.org. 1984. http://thetree.org.uk/BritishTrees/MrsGrieve/mggorse.htm. Accessed 17 March 2008.

Tolera, A., K. Khazaal, E. R. Orskov. 1997. Nutritive evaluation of some browse species. *Animal Feed Sc. Tech*. 67:181-195

Tree Gallery. 2008. http://www.the-tree.org.uk.BritishTrees/TreeGallery/gorsec.htm Accessed 17 March 2008.