PRODUCTION OF LIQUID FUELS AND CHEMICAL FEEDSTOCKS FROM MILKWEED

Robert P. Adams, Ph.D.
Manager, Biomass/Botanochemicals
Plant Resources Institute
360 Wakara Way
Salt Lake City, Utah 84108

DR. ROBERT P. ADAMS
BRACKENRIDGE LABORATORY
UNIVERSITY OF TEXAS
2907 LAKE AUSTIN BLVD.
AUSTIN, TX 78703

ABSTRACT

Alternative sources of fuel and chemical feedstocks from milkweeds. The common milkweeds (Asclepias species)produce hydrocarbons that can be cracked to fuels, possible chemical feedstocks, and a residue (after extraction) that is high in protein and highly digestible. Research during the past two years has centered on agronomy and chemical composition analyses. Agronomic problems are seedling establishment, weed control, harvesting, and storage of material until processing. Many of these problems have now been solved and the agronomic potential for domestication appears very favorable. Chemical analyses has revealed triterpenoids and natural rubber in the hexane extract with polyphenolics, inositol and sucrose in the methanol extract. Additional results are reported on commercial extraction technology. The Asclepias species are compared with other promising hydrocarbon species and problems involved in the domestication of these kinds of species are discussed. These energy crops appear to be economically feasible when a multi-use approach is used but they are not feasible if only the hydrocarbons are utilized.

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INTRODUCTION

The increases in prices of petroleum have generated considerable interest in biomass and botanochemicals as can be seen in a recent volume of Economic Botany (35, 4), which contained three articles on energy crops out of the nine articles published. Calvin (1) has suggested that petroleum plantations might be able to supply some of our future needs. The recent conversions of various hydrocarbon extractives by a zeolite catalyst (2, 3) to liquid fuels further enhances the prospects for this technology. Additional value can be obtained from chemicals for chemical feedstocks which may be extracted from plants (4-6).

The use of the residue (after extraction) is an important economic consideration and naturally leads one to the concept of multi-use (4, 7). In this paper, I would like to present some of the information on a promising hydrocarbon species commonly called milkweed. Although the term milkweed generally refers to any plant that produces a white sap (or latex), I will focus on the genus Asclepias (Asclepiadaceae) and more particularly on Asclepias speciosa Torr., the showy milkweed.

Asclepias speciosa is widely distributed from near the Mississippi River westward to the Pacific Coast, and from Central Saskatchewan and Alberta, southward to central Oklahoma. West of the Rocky Mountains it is chiefly found along irrigation ditch banks. It produces a feathery plume on the seeds and is therefore easily dispersed. In the north-eastern portion of its range (Minnesota), it is competitive with crops and can cause significant problems.

METHODS

The methods used for the extractions have been previously published (5). Ashing was done by standard methods (ASTM D3174-73). Heat values were computed using the ASTM D2015-66 standard method with a Parr 1421 semi-micro calorimeter. Carbon, hydrogen, nitrogen analyses were done on an F & M elemental analyzer at the University of Kansas, Department of Medicinal Chemistry.

RESULTS AND DISCUSSION

Extract Yields and Composition

The yields from Asclepias latifolia (plains milkweed), A. speciosa (showy western milkweed), and A. syriaca (eastern common milkweed) are shown in Table 1. In general the hexane extracts are composed chiefly of triterpenoids (C_{30}) compounds such as alpha- and beta-amyrin. The methanol extracts (polar) are composed of phenolics, flavonoids, free amino acids, and carbohydrates such as sucrose, glucose, and inositol. These analyses are based on samples from specific locations and the results may be quite different at different sites and seasons. Although the plains milkweed (A. latifolia) has the largest yield of hexane extractables, it is a rather poor invader of overgrazed buffalograss and doesn't appear to be very competitive with annual weeds. Asclepias syriaca, being very broadly distributed east of the Mississippi River to the Atlantic Coast, might be developed as a crop in the eastern United States. We are currently concentrating on the development of A. speciosa since it appears to be amenable to cultivation and large areas of semi-arid lands are available in the west for energy plantations. It should be noted that our research, to date, has only utilized seed from local populations and no efforts have been made to select for superior strains nor have any breeding programs been undertaken.

Elemental analyses of the extractives of these three milkweed species are shown in Table 2. The C, H, N analyses for each extract compares closely between the species. Asclepias latifolia does contain somewhat less oxygen in the hexane extractables than the other two species. The gross heat values of the hexane extract are similar to crude oil. The ash contents and gross heat values of the residues are comparable to coal. The most important property of the residue may be the protein (N x 6.25). Although these samples are low in protein (about 10%) it should be noted that these samples were taken late in the growing season after seed was set and the protein content is generally lower at that time (Wayne Craig, personal communication).

Cracking to Liquid Fuels

The heat values of the hexane extracts are quite comparable to crude oil; however, the oxygen content is somewhat higher. These extracts can be cracked to liquid fuels. Table 3 shows a comparison of products obtained from several extractives of different species. The amount of coke ranged from 5% to 12% and seems correlated with fluid bed versus fixed bed. The Grindelia squarrosa extract was obtained by using methylene chloride and is probably higher in oxygenated compounds than hexane extracts. This may account for the large yield of higher molecular weight products (C_{11} and larger) in G. squarrosa.

There is considerable interest in using vegetable oils directly as diesel fuel (10). Whether these non-polar extracts could be blended directly remains to be examined. It is also uncertain whether these non-polar extracts could be co-mingled with crude oil or if they need to be cracked at a separate refinery. The latter case seems most likely.

Utilization of the Polar Extracts

Our research to date on possible utilization of the polar (methanol) extracts has uncovered several possibilities which include: biologically active compounds such as herbicides, fungicides, insecticides, etc.;additives for paints; phenol based intermediates used in chemical synthesis; sugar production and fermentation to ethanol.

Since the polar faction is extremely variable both within and between species, market analysis will be critical before the onset of genetic selection and breeding. Although natural rubber is extracted with the hexane, it seems appropriate to discuss it with special products in this section. Asclepias species are known to produce small amounts of low molecular weight rubber (11). Since our supplies of natural rubber are dependent on imported rubber, political and economic factors may force a reevaluation of the lower molecular weight rubbers. The value of Hevea rubber is several times that of fuels and a rubber fraction may be a very important economic consideration in the future.

Utilization of the Extracted Residue

The milkweed residue (after extraction with hexane and methanol) appears to be non-toxic and equivalent to alfalfa hay in digestibility in sheep (Wayne Craig, personal communication). Asclepias speciosa harvested in full flower (June 26) and extracted (hexane/methanol) was analyzed and found to contain 16.3% crude protein (N x 6.25). This is quite comparable to alfalfa hay (16.0%) and larger than corn grain (9.7 to 10%) (12). Amino acid composition analysis of this June sample revealed (Table 4) that the protein is comparable to alfalfa and generally superior to corn grain. The protein has excellent amounts of lysine (280% of the corn value) and has a greater concentration of the essential amino acids (13) than corn. Only threonine is larger in alfalfa and the milkweed protein is 97.1% in that case. Given a residue that is non-toxic, highly digestible and high in protein, the utilization as a livestock feed appears very promising. This use particularly fits into the agricultural system on the western Great Plains where large feedlots abound. With the increased cost of fuel for pumping irrigation water and the drop in the levels of the Ogalla formation, milkweeds seem to offer an alternative crop for that region.

Agronomic Considerations

Even a very promising species is of only academic interest if it could not be grown. We are expending considerable effort on the agronomic problems associated with this species. An early question arose concerning harvesting methodology. Since the latex is a highly visible reminder of hydrocarbon production (but not a requirement!), we first considered liquid extraction in the field. Table 5 summarizes the results of these experiments (it should be noted that these early experiments were using acetone extracts from young plants and thus are not exactly comparable to the results in Table 1). Notice that only about one third of the oil (mostly tri-terpenoids) was found in the juice (plants were "juiced" in the field) and two-thirds of the oil was left in the pulp. This trend was seen (Table 5) in the rubber and resin (mostly phenolics). The total resin extracted (in juice and pulp) is much larger than obtained from the whole plant. This may be because many of the cells were disrupted during the "juicing" operation and thus the solvent was more efficient in extraction. In any case, it is apparent that the hydrocarbons are sufficiently dispersed throughout the plant that harvesting only the juice or the pulp would result in large losses of products in the field.

Plant biochemistry is constantly changing during the life of a plant. This is often reflected in the accumulation of various compounds. In order to evaluate the ontological effect, eighteen individuals with multiple stems were sampled in full flower (June 26) and later in full fruit development (September 1). A highly significant change occurred in the yields of hexant extracts (Table 6) with an average decrease in yield of 0.49% (whole dry plant basis). This is a relative loss of over 10%. The non-polar compounds may have been converted to polar material since the methanol extract increased (Table 6) from June 28 to September 1 by an average of 0.68% (whole dry plant basis). This change was also highly significant. Analysis of the total extractables of the 18 plants revealed no significant difference. This further implies that interconversions are occurring. A previous study (14) has shown that the non-polar extracts reach a maximum at about full flowering time (late June-early July). Additional studies are being conducted on these seasonal changes.

An important factor in the arid and semi-arid lands is the relationship of water use/stress to biomass and hydrocarbon yields. Our preliminary findings (Table 7) suggest that irrigation did have a significant effect on plant size (in equally spaced plants) in the first harvest (July 28) but no significant effect on the second harvest (August 12). Due to the loss of the lower leaves, the dry weight/plant actually decreased between these two sampling dates. The yield of hexane extractables was 74% larger in the dryland than irrigated plots in the July 28 sample, (irrigated versus dryland 8.09-4.65/4.65) and 34% larger on the August 12 sample (irrigated versus dryland (8.04-5.98)/5.98). These preliminary data suggest that irrigation may not be very important in some areas except as needed to get a crop started insofar as the actual production of hydrocarbons is concerned.

Our principal test field contains 11.5 acres near Syracuse, Utah. Six and one-half acres were seeded in the spring of 1980 by planting two rows (12 inches apart) on top of a bed (36 inches furrow to furrow). Five acres were planted in the spring, 1981, on flat land with a conventional disk-opening grain drill (7" row spacing). Both of these fields have been periodically irrigated to obtain a larger amount of biomass for storage and commercial extraction tests. Although the plant density on the 6.5 acres was too low, it did produce considerable biomass during the second year (1981). Table 8 shows the harvest and regrowth results from 1981. Notice that at the time of 1st cutting (June 29) plants averaged about two stems. This increased to 5.4 stems/plant after the 1st cutting (at the time of the second cutting). A further increase was noted one month after the second cutting (6.3 stems/plant) suggesting that there is a continued, but slowing response to cutting. The yield per acre is not comparable to alfalfa in Utah (3.35 tons/acre) but this may be largely due to the low plant density attained on this plot. One should also note that this seeding utilized seeds obtained from the wild with no selection for vigor nor high yield characteristics.

The first cutting resulted in 2.6 times as many stems per plant but the second harvest increased by only 1.7 times. The plants were definitely shorter the second harvest. Spreading by rhizominous growth is common in many Asclepias species, but has not been very frequent in our test field of A. speciosa. Disking or harrowing the field this winter is expected to promote rhizominous growth and increase the plant density. No data is yet available on the long-term effects of harvesting on these perennial species. However, if they respond similarly to alfalfa, one may expect that reseeding would be needed every five to six years.

Storage. Although alfalfa is often greenchopped and hauled several miles to dehydrating plants, we felt that the economic viability of a new energy/feed crop would be strongest if one could handle the crop like hay or ensilage. Conventional haying practices have been successful. The milkweeds are cut, crimped, and windrowed in one operation. After three to four days, the moisture dropped to 15 to 20%. The windrows were then baled with conventional equipment (Figure 1). A portion of the field was green chopped with a silage cutter and ensilaged. It appears that field drying may result in some loss of the hexane extractables (Table 9) with a corresponding gain in the methanol extractables. This may be due to photolysis, and/or oxidation. The milkweed bales are being stored outside in ambient conditions in Salt Lake City, Utah. Storage tests on the bales have revealed no significant differences in either extracts yields after two months (Table 9). It is likely, however, that the composition of the extracts is changing and this will be reported later. The milkweed silage shows a stable pattern after three months although both samples show a shift of methanol extractables to the hexane extractables (Table 9). This may be due to the degradation of the cell wall infrastructure allowing the hexane (1st solvent) to penetrate more effectively in extraction or direct interconversion. The total yield was very comparable between the bales and the silage.

Comparisons with Other Species. The milkweeds (and latex producing species) are not unique in the production of free hydrocarbons. Table 10 shows results from ten species (5). Many of the species produce greater yields of non-polar extracts (Grindelia, Sapium) than Asclepias. Some produce very large quantities of methanol extractives (Baccharus, Rhus). Euphorbia lathyris has been examined and grown by Diamond Shamrock Corp. (Charles Hinman, personal communication) but is quite susceptible to root rot in time of heat stress. This seriously limits the range where it can be grown with the present genotypes. Grindelia squarrosa is a widely distributed weed in the west that has most of its hydrocarbons on the plant surface. Hess Products, Reno, Nevada (Darrell Lemaire, personal communication) is extracting this species by dipping the plants in methylene chloride. The advantage of that kind of extraction is that residence time in the solvent need only be a few minutes. Calotropis procera is a weedy, tropical shrub/tree that is being examined by ARCO Solar Industries (Robert Inman, personal communication) in the semi-arid parts of Australia. None of the other species are being researched to the author's knowledge.

CONCLUSION

Milkweeds (Asclepias species) offer considerable promise as a multi-use energy/feed crop in the semi-arid lands of the western United States. Although domestication and the introduction into agriculture is probably a decade or more away, this time frame might be compressed if rapid increases in liquid fuel prices occur in the next decade.

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Table 1. Comparison of extract yields from three species of *Asclepias*.

	% Yield Hexane Extract	% Yield Methanol Extract	% Yield Total
A. latifolia	6.31	15.56	21.87
A. speciosa	4.72	18.67	23.39
A. syriaca	3.14	18.66	21.80

Table 2. Characteristics of the extractions and residues of three milkweed species and fossil fuels. Oxygen obtained by substraction.

	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	Ash %	Gross heat cal/g
A. latifolia						
Hexane Extract	80.99	11.87	7.14	0.0	0.0	10427
Methanol Extract	40.44	5.96	52.48	1.18	14.9	4564
Residue	40.30	11.58	46.52	1.60	10.0	3774
A. speciosa						
Hexane Extract	79.16	11.12	9.72	0.0	0.0	10599
Methanol Extract	36.36	5.09	58.55	0.0	21.1	3669
Residue	42.20	5.58	50.62	1.60	9.7	3794
A. syriaca						
Hexane Extract	78.05	11.58	10.07	0.30	0.8	9458
Methanol Extract	44.50	5.80	49.19	0.51	7.6	4158
Residue	38.89	6.40	53.23	1.48	5.1	4338
Anthracite Coal (8)	79.7	2.9	6.1	---	9.6	7156
Lignite Coal (8)	40.6	6.9	45.1	---	5.9	3889
Crude Oil (9)	84.0	12.7	1.2	---	---	10506
Gasoline (9)	84.9	14.76	---	---	---	11528

Table 3. Comparison of cracking products from *Asclepias speciosa* (hexane extract, Craig (personal communication)), *Euphorbia lathyris* (acetone extract, Haag, Rodewald and Weisz (3)), and *Grindelia squarrosa* (methylene chloride extract, Haag, Rosewald and Weisz (3)). The extracts of *E. lathyris* and *G. squarrosa* was subjected to Mobil's ZSM-5, zeolite catalyst.

	A. speciosa	*E. lathyris*		*G. squarrosa*
	Fluid Bed	Fluid Bed	Fixed Bed	Fixed Bed
Products:				
C_1-C_5	11%	27%	10%	15%
Gasoline Range	58	52	36	14
Diesel Range	18	16	42	60
Heating Oil Range	4			
Coke	5	5	12	11
Unaccounted For	4	--	--	--

Table 4. Comparison of amino acid composition of alfalfa, corn grain, and milkweed residue (extracted with hexane and methanol). Amino acids marked with an asterisk are considered essential in non-ruminants (13).

Amino Acid	Alfalfa (12) mg/g	Corn Grain (12) mg/g	*A. speciosa* residue mg/g	% of Alfalfa	% of Corn
alanine	9.9	7.9	8.9	89.9	112.7
arginine*	7.0	4.0	8.9	127.1	222.5
aspartic acid	17.0	2.0	15.8	92.9	790.0
cystine	3.0	1.0	0.9	30.0	90.0
glutamic acid	12.6	27.0	15.3	121.4	56.6
glycine	8.0	5.0	8.7	108.8	174.0
histidine*	3.0	2.0	3.7	123.3	185.0
isoleucine*	8.0	5.0	8.3	103.8	166.0
leucine*	10.0	12.0	14.4	144.0	120.0
lysine*	6.0	3.0	8.4	140.0	280.0
methionine*	1.0	2.0	1.9	190.0	95.0
phenylalanine*	6.0	5.0	8.3	138.3	166.0
proline	8.2	8.0	7.3	89.0	91.3
serine	7.8	1.0	7.2	92.3	720.0
threonine*	7.0	3.0	6.8	97.1	226.7
tryptophan*	1.0	1.0	2.3	230.0	230.0
tyrosine	5.0	5.0	4.2	84.0	84.0
valine*	7.0	5.0	9.6	137.1	192.0

Table 5. Comparison of oils, rubber and resin from whole plants, juice and pulp computed as percents of whole dry plants.

Part	% Oil	% Rubber	% Resin
Whole plant	3.74	0.17	2.28
Juice	1.25	0.05	1.65
Pulp	2.47	0.09	2.21
Juice and pulp	3.72	0.14	3.86

Table 6. Analysis of paired observations of ontological changes in the extractables from eighteen individuals of *Asclepias speciosa*. First samples were taken on June 26 at full flower and the second samples were taken on September 1, during full seed development ($t_{.05}=2.11$; $t_{.01}=2.90$; df=17).

	Hexane Extract % Difference	Methanol Extract % Difference	Total Extract % Difference
Average Difference (June 26-September 1)	0.49	-0.68	-0.20
t-test	7.193 **	3.157 **	0.88 n.s.

Table 7. Effects of irrigation on biomass and hydrocarbon concentration. Data from 12 inch (30 cm) spacings at Alcalde, N.M. Plants collected on the later date (August 12) were lighter due to some losses of lower leaves.

	Dry Plant (g) Weight (± SE)	Percent Yield of Hexane Extractive (± SE)	Hexane Extract Per Plant (g) (Wt. x %)
Harvested (July 28)			
Irrigated	28.18(± 2.07)	4.65 (± 0.09)	131.0
Dryland	15.26(± 1.92)	8.09 (± 0.01)	123.5
Harvested (August 13)			
Irrigated	17.47(± 1.79)	5.98 (± 0.20)	104.5
Dryland	14.34(± 1.31)	8.04 (± 0.26)	115.3

Table 8. Harvest and regrowth data from a 6.5 acre field of *A. speciosa* near Syracuse, Utah.

	1st Cutting June 29	2nd Cutting Sept. 1	Ratio (2nd/1st)	1 Month After 2nd Cutting
Number of Stems/Plant (± SE)	2.07 ± 0.17	5.4 ± 0.60	2.60	6.3 ± 0.59
Dry Weight Yield (lbs./acre)	825	1415	1.72	Not cut

Table 9. Comparison of hexane and methanol yields from field samples, silage, and bales of milkweed.

	Percent Hexane Yield (± SE)	Percent Methanol Yield (± SE)
Whole plant, oven dried (25)	5.00 ± 0.092	13.96 ± 0.35
Milkweed bales (5) 1 week after baling	4.19 ± 0.076	18.48 ± 0.680
after 1 month of storage	4.07 ± 0.072	18.33 ± 0.675
after 2 months of storage	4.14 ± 0.308	18.90 ± 1.02
Silage (1), after 1 month	5.89	15.83
Silage (1), after 3 months	5.81	15.28

Table 10. Comparison of the yields of extractables of several important terpenoid species (data from Adams and McChesney (5)).

Plant Species	Hexane % Yield	Methanol % Yield	Total % Yield
Asclepias speciosa	4.72	18.67	23.39
Baccharus neglecta	5.20	27.35	32.55
Calotropis procera	4.66	16.78	21.44
Coreopsis tinctoria	3.40	21.65	25.05
Euphorbia lathyris	6.61	19.13	25.74
Grindelia squarrosa	12.00	10.52	22.52
Rhus glabra	6.35	46.20	52.55
Sapium sebiferum	10.30	22.40	32.70
Solidago microcephala	7.45	16.70	24.15
Trepocarpus aethusae	7.45	20.08	27.53